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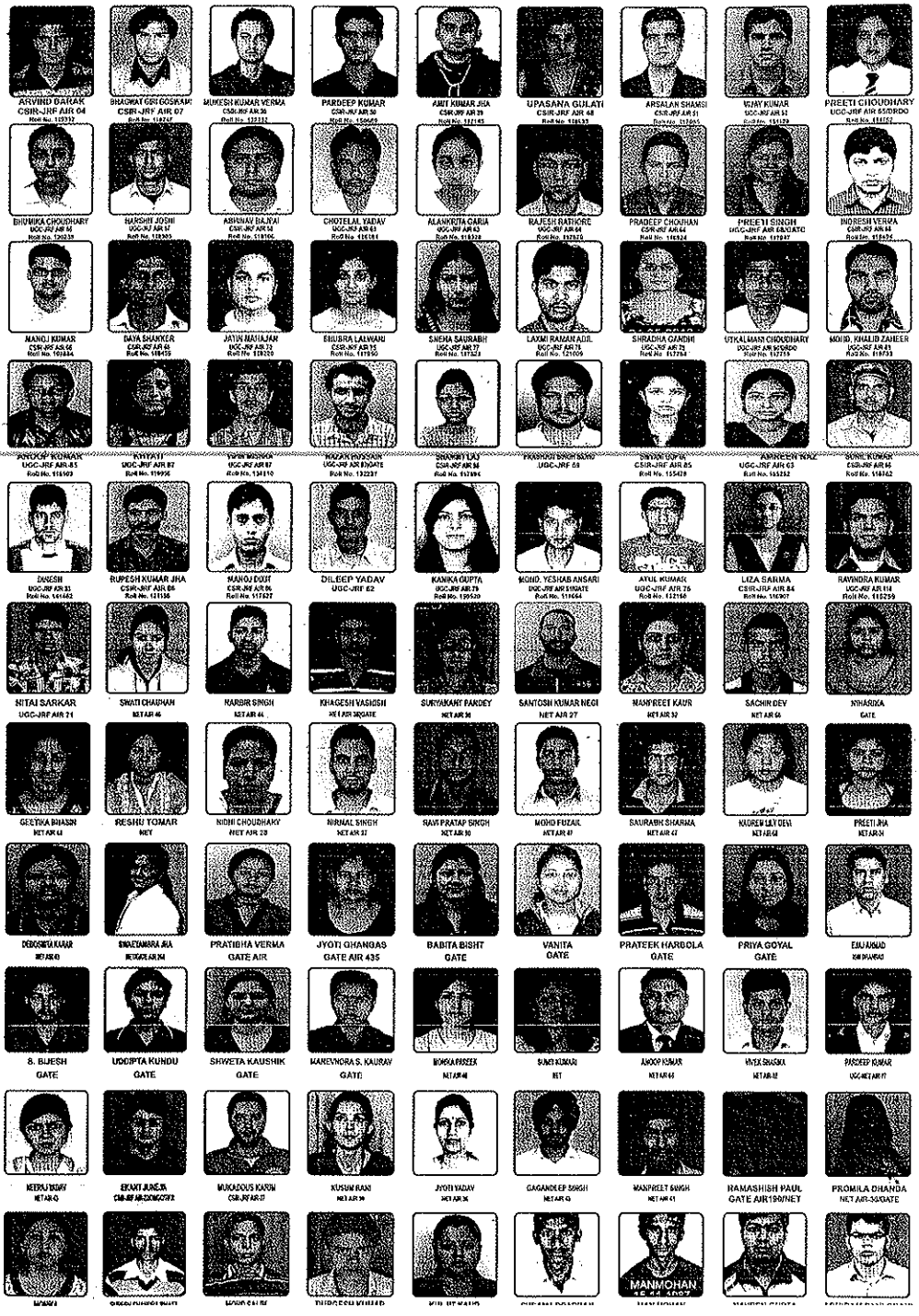

GROUP THEORY

for

CSIR-UGC-NET/JRF|GATE

TIFR | BARC | IISc | DRDO | SLET | NTPC | ONGC-GT | HPCL | Ph.D Entrance

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GROUP THEORY

1. Element of symmetry
2. Calculation of elements,
3. Point groups
4. Application of elements on axis x, y, z and matrix of each element.
5. **Representation :**
   1. Reducible
   2. Irreducible
   3. Derivation of character table.
6. **Application :**
   1. **Hybridisation :** For mixing of orbital having same symmetry and having same energy.
   2. IR/ Raman/ Microwave are also explained by group theory.

SYMMETRY :

Some tools for defining the symmetry like.

1. **Symmetry Elements :** There are 3 elements.
   (i) axis of symmetry
   (ii) Plane of symmetry
   (iii) centre of symmetry

Elements of symmetry	Operation of symmetry elements
Axis of symmetry	Rotation C_n operation
Plane of symmetry	Reflection, σ operation
Improper axis of symmetry	Rotation-Reflection, S_n operation
Centre of Symmetry	Inversion (i)
Identity	Nothing to do for E

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ELEMENT OF SYMMETRY :

Geometrical entity on the basis of that we can define the symmetry of an object is known as element of symmetry like, Axis, Plane, Point, etc.

OPERATION OF SYMMETRY ELEMENT :

Operation of symmetry element is the process which we apply on the element to define the symmetry.

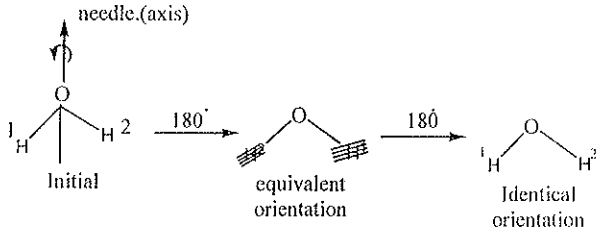
1. **Axis of Symmetry :**

Imaginary axis passing through the molecule rotation on which by $()^0$ gives an equivalent orientation.

Orientation of Molecule : 3D distribution of atoms of the molecule is called orientation two type of orientation of molecule.

(i) Identical Orientation :

The orientation of initial molecule through the equivalent orientation by which we get the same or exact identical molecule representation.



(ii) Equivalent Orientation :

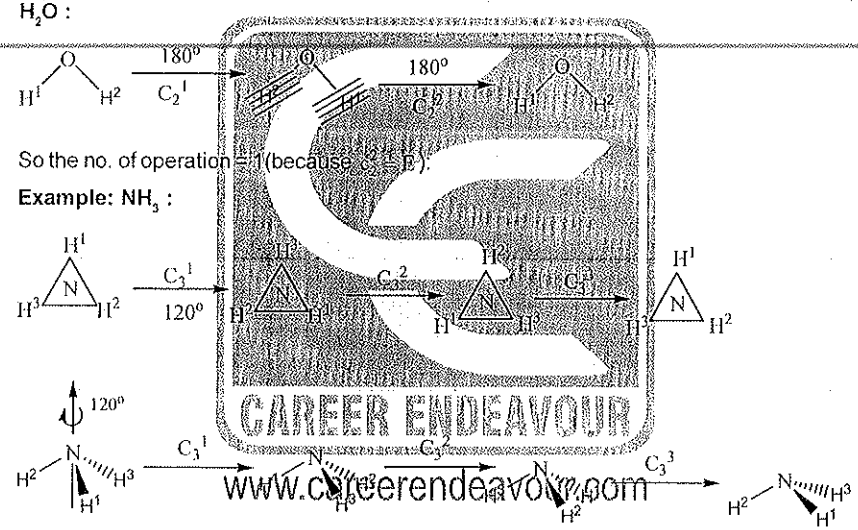
C_n OPERATION :

$$n = \frac{360}{\theta} = \frac{360}{180} = 2$$ Order of axis - C_2 axis

NUMBER OF OPERATION :

Number of operation to find the identical orientation (identity) . i.e.

H_2O :



So the no. of operation = 1 (because $C_2^1 = E^1$).

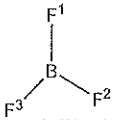
Example: NH_3 :

Order of axis = $\frac{360}{120} = 3 \rightarrow C_3$ axis

Number of operation = 2 because C_3^3 is identity.

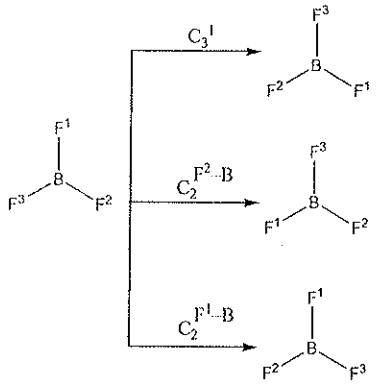
Example: BF_3 : 3 C_2 axis and 1 C_3 axis.

3 C_2 axis :

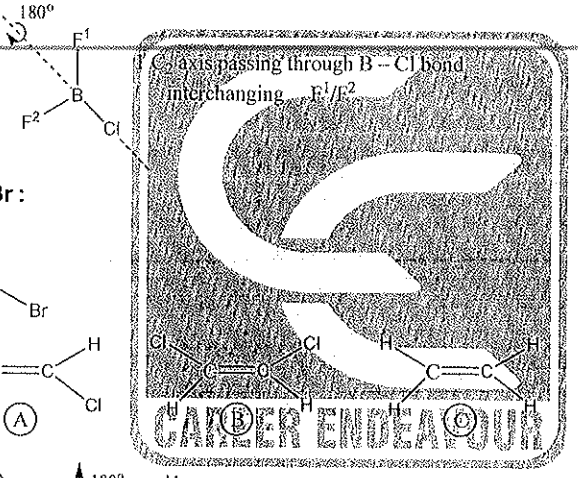


1. C_2 axis passing through F^1 – B bond and interchanging F^2/F^3.
2. C_2 axis passing through F^2–B bond and interchanging F^1/F^3.
3. C_2 axis passing through F^3–B bond interchanging F^1/F^2.

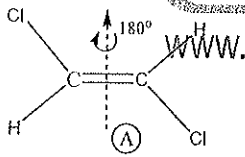
$1C_3$ AXIS : C_3 axis passing through B atom and $\perp$ to each C_2 axis.



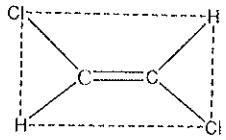
BF_2Cl :



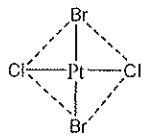
BFClBr :



Plane passing through double bond of carbon or mid point of C=C $\perp$ to molecular plane



Rectangle



Square

C_2 is not present at diagonal in rectangle structure.

C_2 present at diagonal in square planar structure

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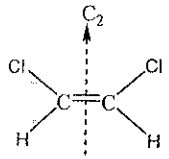
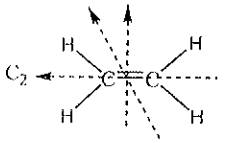
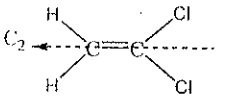


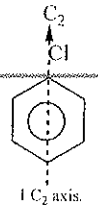
C_2 passing through mid point of C = C within the molecular plane.



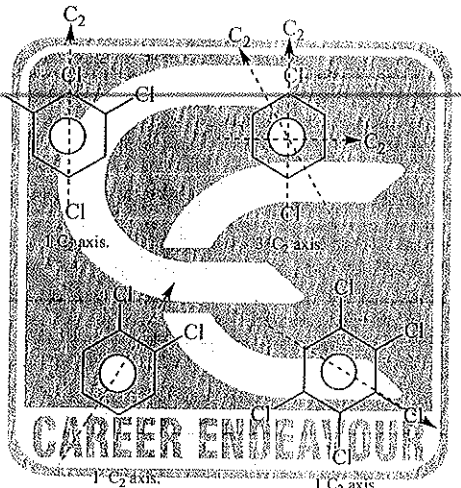
3 C_2 axis perpendicular to each other



One C_2 axis.



1 C_2 axis.



1 C_2 axis. 1 C_2 axis. 3 C_2 axis. 1 C_2 axis. 1 C_2 axis.

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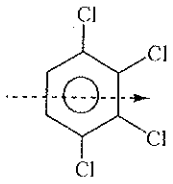
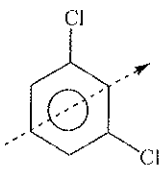
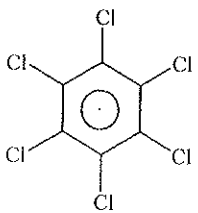
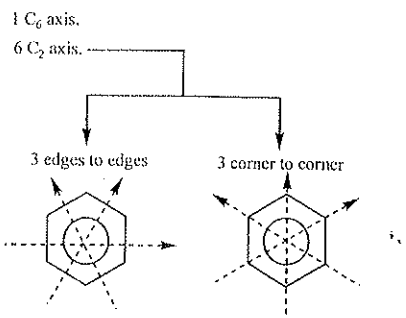


1 C_2 axis.

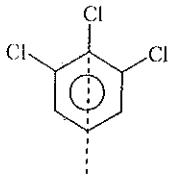


1 C_2 axis.

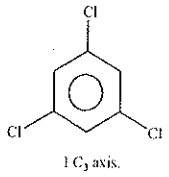




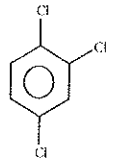
1 C_6 axis.
6 C_2 axis.
3 edges to edges
3 corner to corner



1 C_2 axis.



1 C_3 axis.
3 C_2 axis



No axis

NUMBER OF SYMMETRY OPERATION :

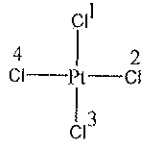
$C_2 \longrightarrow C_2^1 = 1$

$C_3 \longrightarrow C_3^1, C_3^2 = 2$

$C_4 \longrightarrow C_4^1, C_4^2, C_4^3 = 3$

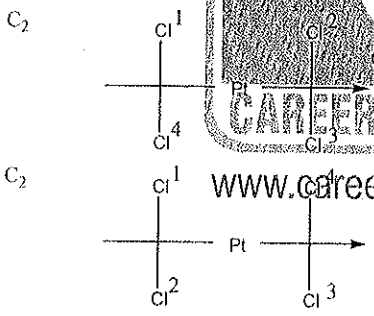
$C_5 \longrightarrow C_5^1, C_5^2, C_5^3, C_5^4 = 4$

D_{4h} Point Group:



$K_4 + 4C_2$

4 C_2 axis.
C_2 passing through $Cl^1 - Pt - Cl^3$
C_2 passing through $Cl^2 - Pt - Cl^4$



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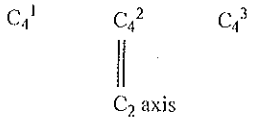
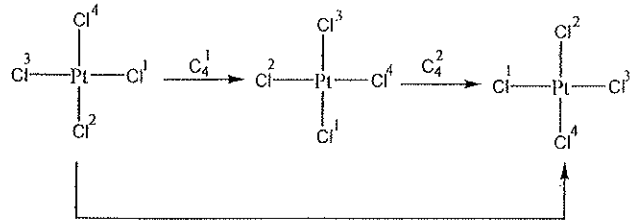
1C_4 AXIS : C_4 passing through Pt $\perp$ all C_2 axis



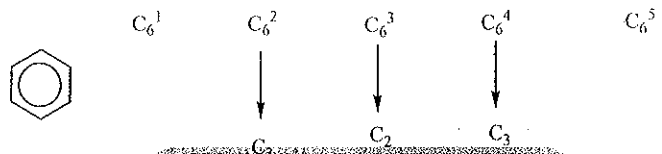
C_4^1 C_4^2 C_4^3

C_2 axis



$180^0 = C_2$

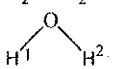
$C_4^2 = C_2$



2. PLANE OF SYMMETRY :

Imaginary plane passing through the molecule which can bisect into two mirror image halves. eg:

H_2O : $C_2 + 2\sigma$:



Two planes

(1) σ bisecting O and reflecting H^1 and H^2

(2) σ bisecting H^1—O—H^2

AXIS :

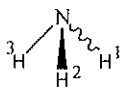
1 C_2 axis passing through O & interchange $\frac{H^1}{H^2}$:

NH_3 :

$C_3 + 3\sigma$

NH_3 has 3 planes.

Plane :



σ bisecting N—H^1 reflecting $\frac{H^2}{H^3}$

bisecting N—H^2 reflecting $\frac{H^1}{H^3}$

bisecting N—H^3 reflecting $\frac{H^1}{H^2}$

Axis :

C_3 axis passing through N atom along with three planes.

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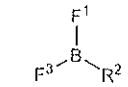
Plane :



σ bisecting B—F^1 reflecting $\frac{F^2}{F^3}$

σ bisecting B—F^2 reflecting $\frac{F^1}{F^3}$

σ bisecting B—F^3 reflecting $\frac{F^1}{F^2}$

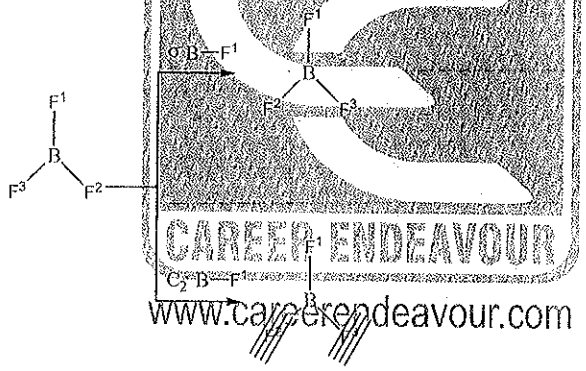
σ bisecting all 4 atoms.

Axis : C_1 passing through B—F^1 interchanging $\frac{F^2}{F^3}$

C_2 passing through B—F^2 interchanging $\frac{F^1}{F^3}$

C_3 passing through B—F^2 interchanging $\frac{F^1}{F^3}$

C_3 passing through B $\perp$ to all C_2 axis or molecular plane :



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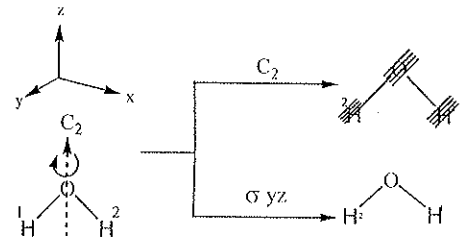
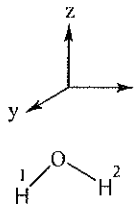
BASIC DIFFERENCE BETWEEN C_2 AND PLANE: σ or plane does not change the face of reflecting atoms while C_2 changing the atoms along with its faces.



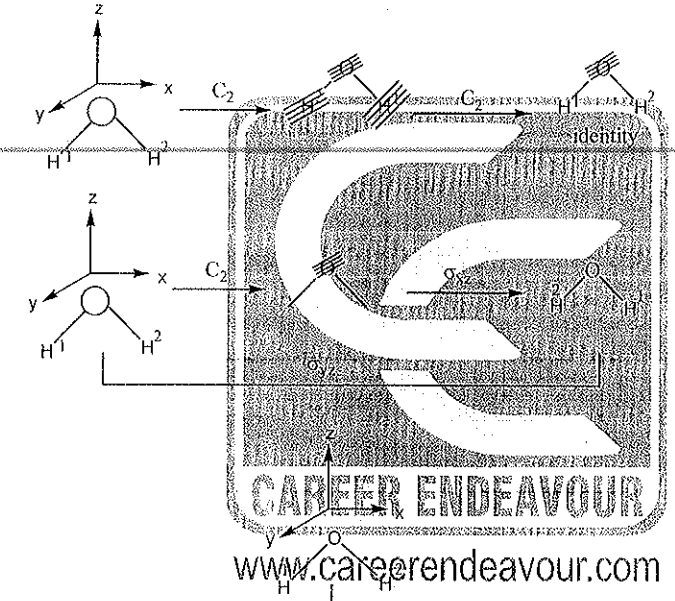
GROUP MULTIPLICATION TABLE OF H_2O :

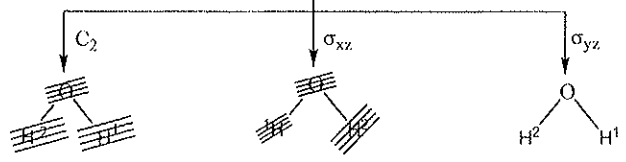
H_2O	E	C_2	σ_{xz}	σ_{yz}
E	E	C_2	σ_{xz}	σ_{yz}
C_2	C_2	E	σ_{yz}	σ_{xz}
σ_{xz}	σ_{xz}	σ_{yz}	E	C_2
σ_{yz}	σ_{yz}	σ_{xz}	C_2	E

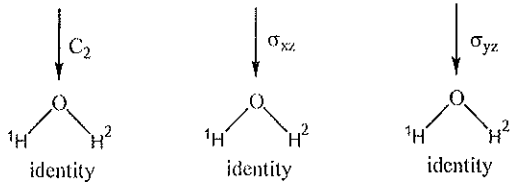


$E \times E = E$
$C_2 \times E = C_2$
$\sigma_{xz} \times E = \sigma_{xz}$
$\sigma_{yz} \times E = \sigma_{yz}$
$C_2 \times C_2 = E$
$C_2 \times \sigma_{xz} = \sigma_{yz}$
$\sigma_{xz} \times \sigma_{xz} = E$
$\sigma_{yz} \times \sigma_{yz} = E$

Identity (E) does not affect any symmetry element.







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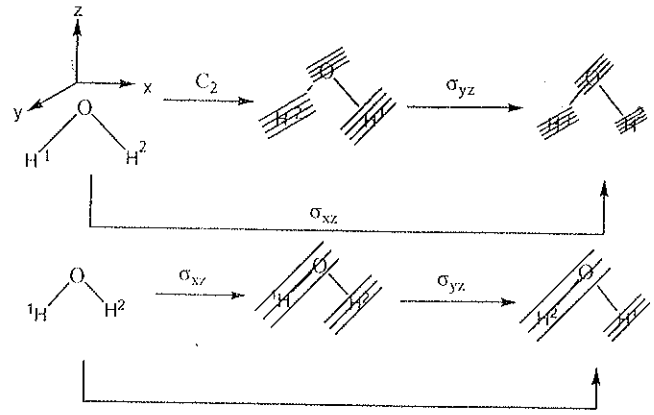
Always plane affect when it use odd times, but it give identity when it use even times.



CLASSIFICATION OF AXIS OF SYMMETRY

Axis

Principal Axis (P-axis)

Axis of highest order
n = order of axis
e.g. BF_3 : C_3 is P-axis

Subsidiary Axis (S-axis)

Axis other than P-axis
3 C_2 are S-axis

CLASSIFICATION OF PLANE OF SYMMETRY

Plane

Vertical Plane σ_v

Plane ∥ to P-axis

Horizontal Plane σ_h

Plane $\perp$ to P-axis

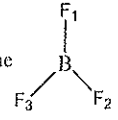
Dihedral Plane σ_d

Plane ∥ to P-axis and bisecting angle between two C_2 axis in the molecule.

Plane in BF_3

σ BF^1
σ BF^2
σ BF^3
} $3\sigma_v$

1 σ_h i.e. molecular Plane



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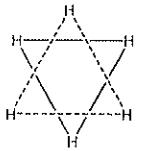
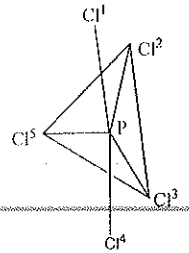
Eg : Staggered Ethane : $3\sigma_d$



PCl_5 : $1C_3, 3C_2, 3\sigma v, 1\sigma h$

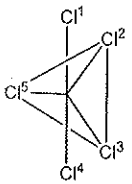


1 C_3 axis : Passing through. Cl^1–P–Cl^4

3 C_3 axis :

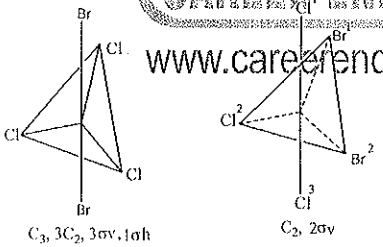
C_2 Passing through.	P——Cl^2	interchanging	Cl^1/Cl^4
C_2 Passing through.	P——Cl^3	interchanging	Cl^1/Cl^4
C_2 Passing through.	P——Cl^5	interchanging	Cl^1/Cl^4

Planes :



σ_v bisecting	$Cl^1\ Cl^2\ Cl^4\ P$	reflecting	Cl^3/Cl^5
σ_v bisecting	$Cl^1\ Cl^3\ Cl^4\ P$	reflecting	Cl^2/Cl^5
σ_v bisecting	$Cl^1\ Cl^5\ Cl^4\ P$	reflecting	Cl^2/Cl^3
σ_v bisecting	$Cl^2\ Cl^3\ Cl^5\ P$	reflecting	Cl^1/Cl^4

In PCl_5 replace 2Cl with 2 Br and Keep all elements as such.



$C_3, 3C_2, 3\sigma v, 1\sigma h$

$C_2, 2\sigma v$

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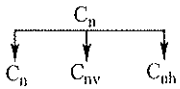
1. C_{nv} Point Group :

$C_{nV} = C_n + n\ \sigma_V$



eg :

$C_{2V} = C_2 + 2\ \sigma_v$ no. of operation = 2n = 4

$C_3V = C_3 + 3\sigma_v$ no. of operation = 2n = 6

$C_{4V} = C_4 + 4\sigma_v$ no. of operation = 2n = 8

Total no. of operation of elements = order of group = 2 n

(2) C_{nh} Point Group : $C_{nh} = C_n + \sigma_h$

eg :

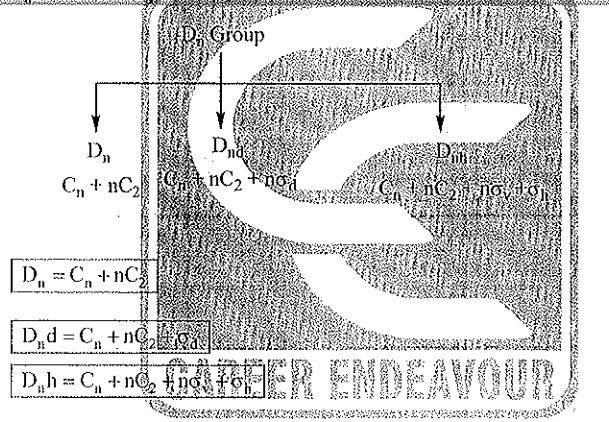
$C_{2h} = C_2 + \sigma_h$ no. of operation = 2n = 4

$C_{3h} = C_3 + \sigma_h$ = 6

$C_{4h} = C_4 + \sigma_h$ = 8

- Total no. of operation is known as order of group.

(3) D_n Point Group : no. of operation = 4n



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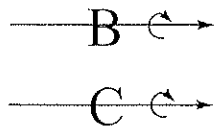
- Any molecule having either $1C_2$ or $3C_2$ not having $2C_2$ always.

$C_2, 2\sigma_v = C_{2v}$



$C_2, 2\sigma_v = C_{2v}$

$C_2, 2\sigma_v = C_{2v}$

$C_2 \times 2\sigma_v = C_{2v}$

$C_2 \times 2\sigma_v = C_{2v}$

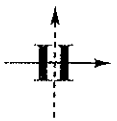
F

C_s only plane of symmetry

G

C_s

The molecule having only one plane not any axis then called they fall in C_s point group.



$3C_2 + 2\sigma_v + \sigma_h$

$C_2 + 2C_2 + 2\sigma_v + \sigma_h = D_{2h}$

I

$C_2 + 2C_2 + 2\sigma_v + \sigma_h = D_{2h}$

J

C_s

K

$C_2, 2\sigma_v = C_{2v}$

L

C_s

M

$C_2, 2\sigma_v = C_{2v}$

N

$C_2 + \sigma_h = C_{2h}$

O

$C_\infty + \infty C_2 + \infty\sigma_v + \sigma_h = D_{\infty h}$

$C_n = \frac{360}{\theta} = n$

C_∞ $n = \infty$ n = because 0° is so much small then $n = \infty$

P

C_s

Q

C_s

R

C_s

S

$C_2 + \sigma_h = C_{2h}$

T

$C_2 + 2\sigma_v = C_{2v}$

U

$C_2 + 2\sigma_v = C_{2v}$

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V

$C_2 + 2\sigma_v = C_{2v}$

W

$C_2 + 2\sigma_v = C_{2v}$

X

$C_4 + 4C_2 + 4\sigma_v + \sigma_h = D_{4h}$

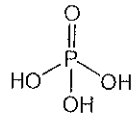
Y

$C_2 + 2C_2 + 2\sigma_v = C_{3v}$

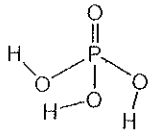
Z

$C_2 + \sigma_h = C_{2h}$

Example: H_3PO_4



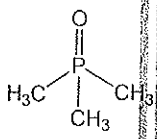
C_3



(Actual Structure)

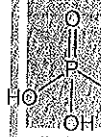
We will state the point group of any molecule in its highest stable arrangement.

Example:



Consider CH_3 as a point then point group C_{3V}.

Example:



Consider OH as a point then point group C_{3V}.

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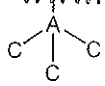
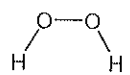
means



Type molecule

EXAMPLE: H_2O_2 :

Having 3 structures - Cis, Trans, Open book

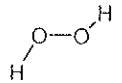


Cis

$C_2 + 2\sigma_v = C_{2v}$

dihedral angle = 0

C is having no dihedral angle

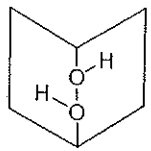


Trans

$C_2 + \sigma_h = C_{2h}$

dihedral angle = 180°

Trans having many dihedral angle.



C_2 point group

Angle formed between Cis and Trans all known as Dihedral angle.

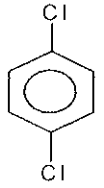
Maximum time H_2O_2 exist as open book

structure having C_2 point group.

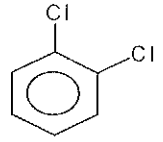
Cis H_2O_2 having C_{2v} point group.

Trans H_2O_2 having C_{2h} point group.

Example:

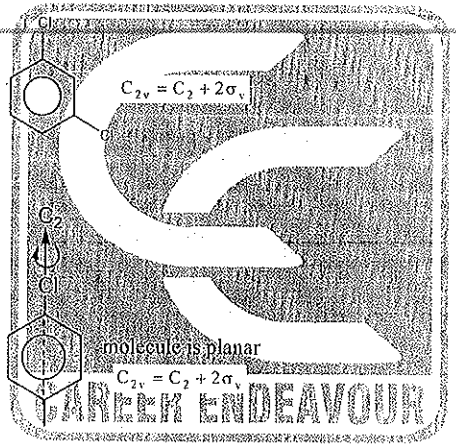


$D_{2h} = C_2 + 2C_2 + 2\sigma_v + \sigma_h$



$C_{2v} = C_2 + 2\sigma_v + h$

Example:



Example:

molecule is planar

$C_{2v} = C_2 + 2\sigma_v$

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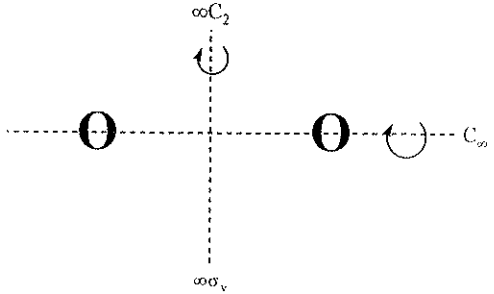
HOMODIATOMIC MOLECULE

O_2

Cl_2:

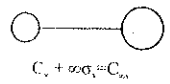
H_2:



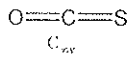
$C_\infty + \infty C_2 + \infty\sigma_v + \sigma_h = D_{\infty h}$

HETERODIATOMIC MOLECULE

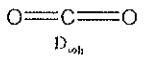
HCl :



$C_v + \infty\sigma_v = C_{\infty v}$



$C_{\infty v}$



$D_{\infty h}$

OZONE

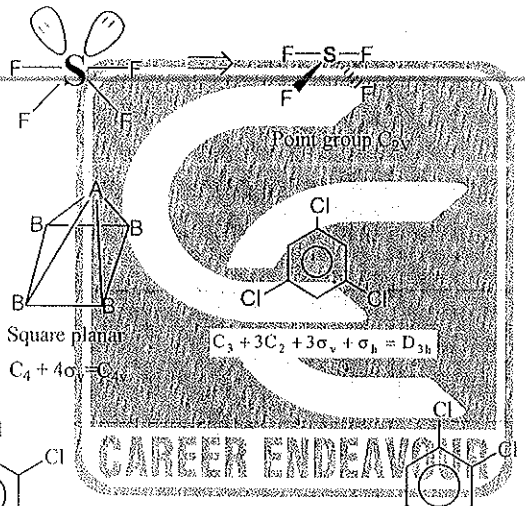
C_{2v}

I_3

linear

$D_{\infty h}$

Example: $SF_4 : C_{2V}$



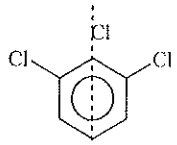
Point group C_{2v}

Example:

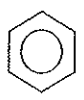
Square planar

$C_4 + 4\sigma = C_{4v}$

$C_3 + 3C_2 + 3\sigma_v + \sigma_h = D_{3h}$

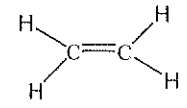


$C_{2v} = C_2 + 2\sigma_v$

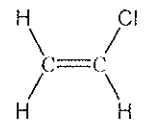


$C_6 + 6C_2 + 6\sigma_v + \sigma_h = D_{6h}$

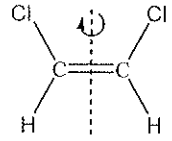
C_s



$C_2 + 2C_2 + 2\sigma_v + \sigma_h = D_{2h}$



C_s



$C_2 + 2\sigma_v = C_{2v}$

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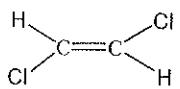
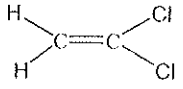


$C_2 + \sigma_h = C_{2h}$



$C_2 + 2\sigma_v = C_{2v}$

$D_{2h} = C_2 + 2C_2 + 2\sigma_v + \sigma_h$

IMPROPER AXIS OF ROTATION

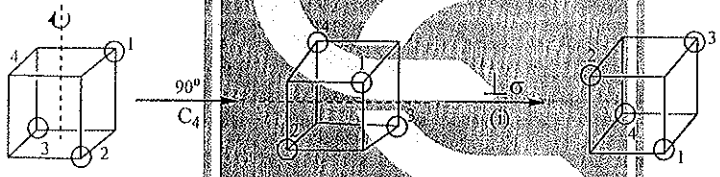
Roto Reflection Axis(Sn) :

Initial $\xrightarrow{\theta^\circ \text{ rotation}}$ $\xrightarrow{\perp \sigma}$ equivalent orientation

CH_4 has, S_4 axis of rotation

Initial $\xrightarrow{90^\circ}$ $\xrightarrow{\perp \sigma}$ Equivalent

CH_4 has tetrahedral structure. If we place CH_4 molecule in a cube then the four atom touches the four corners of the cube. CH_4 having S_4 it doesn't mean that C_4 must also be there.



$$\eta = \frac{360^\circ}{90^\circ} = 4$$

So S_4

$Ch \rightarrow (n-1)$ operation

$C_2 \rightarrow 1$ operation

$C_3 \rightarrow 2$ operation

$C_4 \rightarrow 3$ operation

$C_5 \rightarrow 4$ operation

Number of Operation in Sn Axis :

$S_2 \quad C_2 \perp \sigma$

$S_3 \quad C_3 \perp \sigma$

$S_4 \quad C_4 \perp \sigma$

$S_5 \quad C_5 \perp \sigma$

$\sigma_{odd} = \sigma$

$\sigma_{even} = E$

$C_2^1 \times \sigma^1 = C_2^1$

$C_2^2 \times \sigma^2 = E$

$C_3^1 \times \sigma^1 = S_3^1$

$C_3^2 \times \sigma^2 = C_3^2 \times E = C_3^2$

$C_3^3 \times \sigma^3 = \sigma$

$C_3^4 \times \sigma^4 = C_3^1$

$C_3^5 \times \sigma^5 = C_3^5 \times \sigma = S_3^5 = S_3^2$

$C_3^6 \times \sigma^6 = E \times E = E$

S_5 :

$C_5^1 \times \sigma^1 = S_5^1$

$C_5^2 \times \sigma^2 = C_5^2$

$C_5^3 \times \sigma^3 = S_5^3$

$C_5^4 \times \sigma^4 = C_5^4$

$C_5^5 \times \sigma^5 = \sigma = E \times \sigma = \sigma \quad S_5^1\ S_5^2\ S_5^3\ S_5^4$

$C_5^6 \times \sigma^6 = C_5^1$

$C_5^7 \times \sigma^7 = C_5^2 \times \sigma = S_5^2$

$C_5^8 \times \sigma^8 = C_5^3$

$C_5^9 \times \sigma^9 = C_5^4 \times \sigma = S_5^4$

$C_5^{10} \times \sigma^{10} = E$

$\sigma^2 = \sigma^4 = \sigma^6 = E$

$C_2^2 = C_3^3 = C_4^4 = E$

$E \times X = X$

$\sigma^5 = \sigma^4 \times \sigma$

$= E \times \sigma = \sigma$

S_6 :

$C_6^1 \times \sigma^1 = S_6^1$

$C_6^2 \times \sigma^2 = C_6^2$

$C_6^3 \times \sigma^3 = S_6^3$

$C_6^4 \times \sigma^4 = C_6^4$

$C_6^5 \times \sigma^5 = S_6^5$

$C_6^6 \times \sigma^6 = E$

Some Imperical Points :

Case : I. If n is even then $C_{n/2}$ axis will exist.

Case : II. n is odd then C_n will exist.

e.g. : S_4 CH_4 C_2 will exist

S_{10} C_6H_6 C_5 will exist

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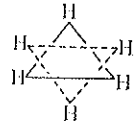
Q. **A molecule have C_2 axis and a perpendicular plane what will be the point group. The possibility is for C_{nh} and D_{nh}.**

- **If molecule having only one C_2 then ans is C_{2h}.**
- **There is not given how many C_2 in this given molecule, so the point group may be D_{2h}.**

Example: STAGGERED ETHANE :

$1C_3$ axis, $3C_2$ axis, $3\sigma_d$

$C_3 + 3C_2 + 3\sigma_d = D_{3d}$



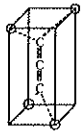
Ethane having H_2O_2 like structure, so having $3C_2$ axis.

The plane bisect the angle formed by the $2C_2$ So Ethane (Staggered) having 3 dihedral plane. Here C_2 does not exist where plane is passes.

Example:

ALLENES : Allenes are elongated tetrahedran.

$C_2 + 2C_2 + 2\sigma_d = D_{2d}$



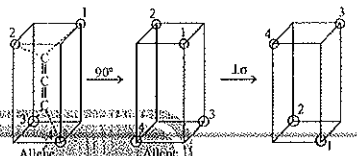
both C_2 having 90° angle and both dihedral plane having 90° angle.

Number of operation in D_{2d} point group:

Total no. of operation = 4 n = 4 × 2 = 8

So, it having

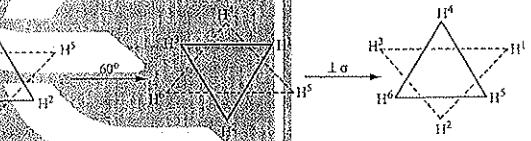
$3C_2$	→	3
$2\sigma d$	→	2
E	→	1
		8



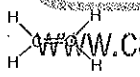
Number of operation in D_{3d} :

$4n = 4 \times 3 = 12$

$1C_3$	→	2
$3C_2$	→	3
$3\sigma_d$	→	3
E	→	1
S_6	→	3
		12



ECLIPSED DOUBLE BOND SYSTEM

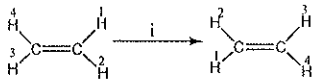


$C_2 + 2C_2 + 2\sigma_v + \sigma_h = D_{2h}$

No. of total operation = 4 × n = 4 × 2 = 8

Explanation :

$1C_2$	→	1
$2C_2$	→	2
$2\sigma_v$	→	2
σ_h	→	1
E	→	1
i	→	1



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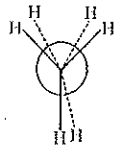
ECLIPSED ETHANE : $C_3 + 3C_2 + 3\sigma_v + \sigma_h = D_{3h}$

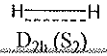
No. of total operation = 4n = 4 × 3 = 12



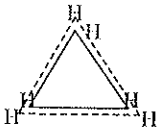
Explanation :

$1C_3$	→	2
$3C_2$	→	3
$3\sigma_v$	→	3
σ_h	→	1
E	→	1
S_3	→	2
		12

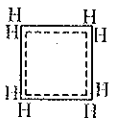
Eclipsed **Staggered**



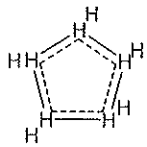
D_{2h} (S_2)



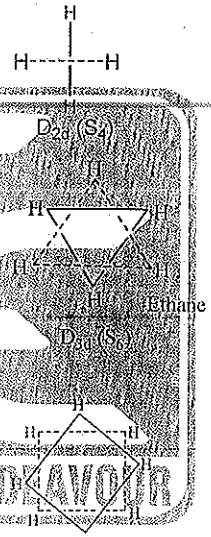
Ethane
D_{3h} (S_3)



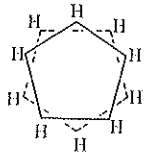
D_{4h} (S_4)
Cyclobutane



D_{5h} (S_5)
Ferrocene



D_{4d} (S_8)
Cyclobutane



D_{5d} (S_{10})
Ferrocene

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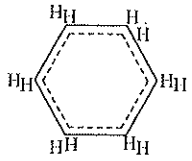
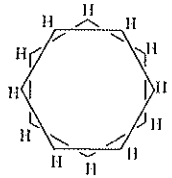
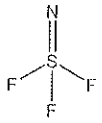


D_{6h} (S_6)
Dibenzene chromium



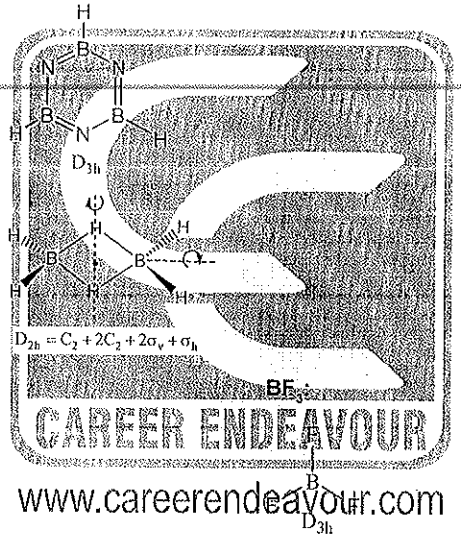
D_{6d} (S_{12})
Dibenzene chromium

NSF_3 : C_{3v} :



C_{3v}

BORAZINE :

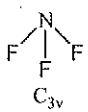


D_{3h}

B_2H_6 :

$D_{2h} = C_2 + 2C_2 + 2\sigma_v + \sigma_h$

NF_3 :



C_{3v}

BF_3 :

D_{3h}

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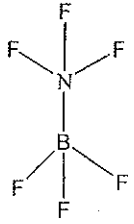
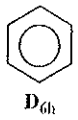
Example:



C_{3V}

C_2 is not found here because both central atoms are different

BENZENE :

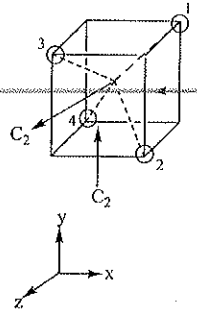


D_{6h}

TOTAL OPERATION = 4N = 4 × 6 = 24

C_6	=	5	$C_6^1 \times \sigma^1 = S_6^1$
$6C_2 = 6$			$C_6^2\sigma^2 = C_6^2$
$6\sigma_v$	=	6	$C_6^3\sigma^3 = S_6^3 = S_2$
σ_h	=	1	$C_6^4\sigma^4 = C_6^4$
S_6	=	2	$C_6^5\sigma^5 = S_6^5$
S_3	=	2	$C_6^6\sigma^6 = E$
$S_2 = i$	=	1	
E	=	1	
		24	

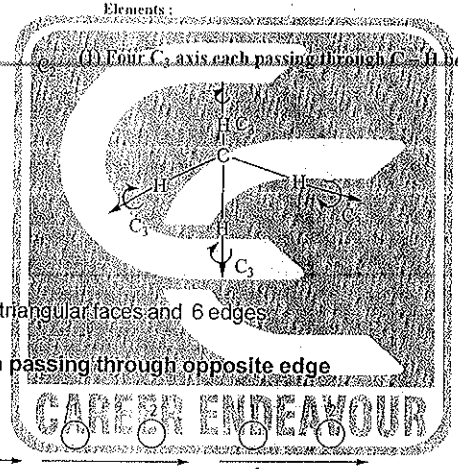
TETRAHEDRON (Td) i.e. 4 triangular face, order of group = 24



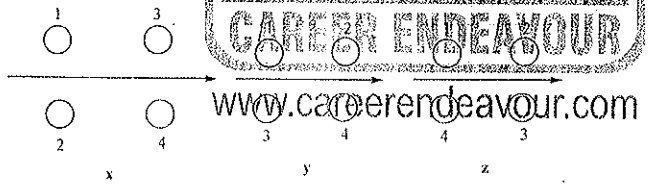
Tetrahedron have 4 triangular faces and 6 edges.

Elements :

(1) Four C_3 axis each passing through C – H bond

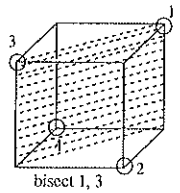


2. **Three C_2 axis each passing through opposite edge**

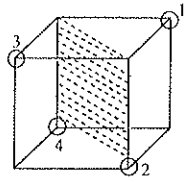


3. **Six plane of symmetry - σ_d :**

each σ_d passing through edges.



bisect 1, 3
reflect 4, 2



bisect 2, 4
reflect 1, 3

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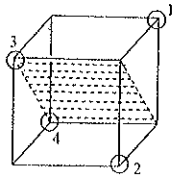
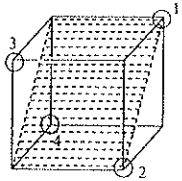
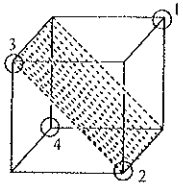


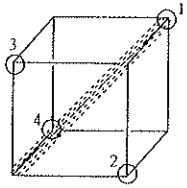
bisect 3, 4
reflect 1, 2



bisect 1, 2
reflect 3, 4



bisect 2, 3
reflect 1, 4



bisect 1, 4
reflect 2, 3

4. Three S_4 axis = 6
5. Identity = 1

1. Four C_3 axis each passing through C–H bond = 8
2. Three C_2 axis each passing through opposite edges = 3
3. Six plane of symmetry σ_d = 6
4. Three S_4 axis = 6
5. Identity = 1

24

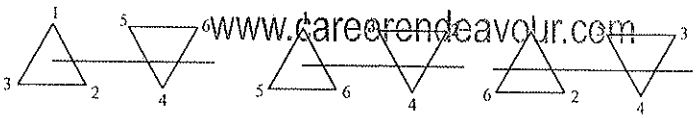
OCTAHEDRON (Oh)

Octahedron having 8 triangular faces

Order of group = 48

12 edges

6 corner



ELEMENT:

1. 3 C_4 axis passing through opposite corner ⊥ to each other
2. 4 C_3 axis passing through opposite triangular face= 8
3. 6 C_2 axis passing through opposite edges = 9

It having 3 principle C_4 axis So it having 3 σ_h plane.

Plane :

4. 3 σ_h = 3
5. 6 σ_h = 6

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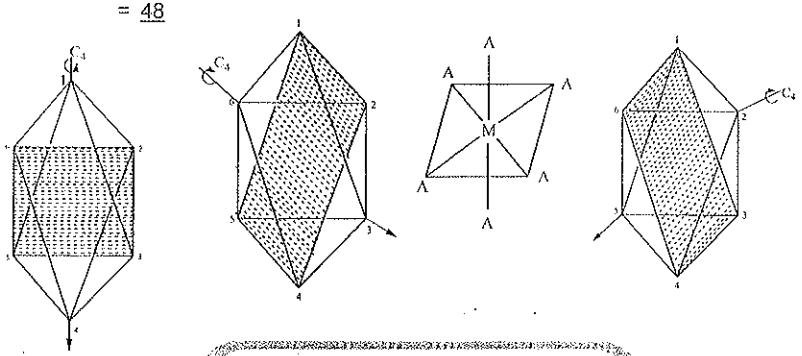
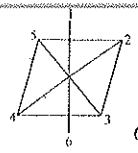
6. 3 S_4 each along with C_4 axis = 6
7. 4 S_6 each passing through opposite staggered triangle = 8
8. Identity E = 1
9. Inversion = 1

= 48

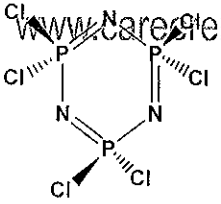




6 σ_d plane

B	R
(1) 1, 6	2/5 and 3, 4
(2) 1, 6	2/3 and 5/4
(3) 3, 5	1/2 and 4/6
(4) 3, 5	1/4 and 2/6
(5) 2, 4	1/5 and 3/6
(6) 2, 4	1/3 and 5/6

Example: $N_3P_3Cl_6$: D_{3h}



$D_{3h} = C_3 + 3C_2 + 3\sigma_v + \sigma_h$

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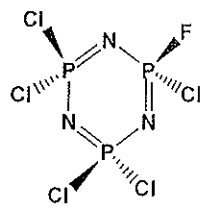
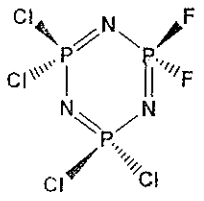
Example: $N_3P_3FCl_5$ $N_3P_3F_2Cl_4$



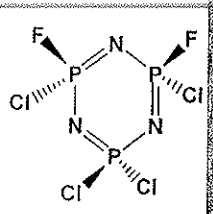
C_s

Only one plane not any axis.

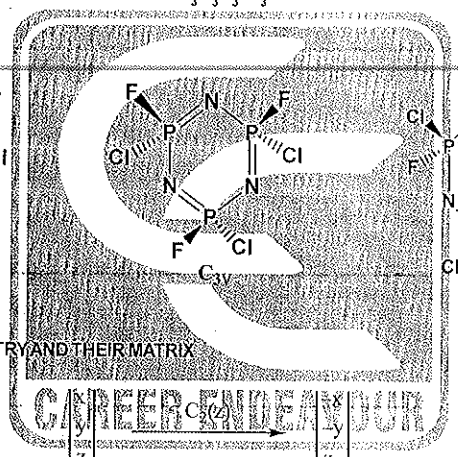


$C_{2V} = C_2 + 2\sigma_v$

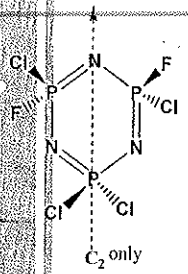
$N_3P_3F_2Cl_4$ $N_3P_3F_3Cl_3$ $N_3P_3F_2Cl_4$



C_s only

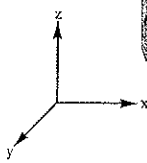


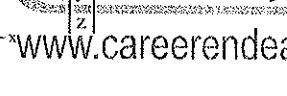
C_{3V}



C_2 only

ELEMENT OF SYMMETRY AND THEIR MATRIX





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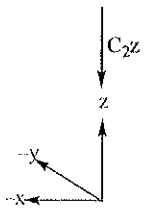


	x	y	z
x	1	0	0
y	0	1	0
z	0	0	1

[x is orthogonal to y & z and normal to x]
Therefore, xx=1
& xy = 0 = xz

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \xrightarrow{C_2(z)} \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

Character x = – 1

X = 3
identity

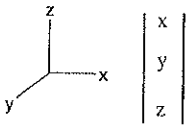
Element

The sum of diagonal elements is called character

Matrix for C_2:

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad x = -1$$

Matrix for Plane :



$$\begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{\sigma_{xz}} \begin{vmatrix} x \\ -y \\ z \end{vmatrix} \qquad \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad x = 1$$

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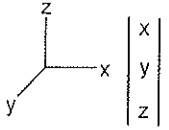
$$\begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{\sigma_{yz}} \begin{vmatrix} -x \\ y \\ z \end{vmatrix} \qquad \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad x = 1$$

Inversion = $S_2 = C_2 \perp \sigma$



$$\begin{vmatrix} x \\ y \\ z \end{vmatrix} \xrightarrow{C_2(z)} \begin{vmatrix} -x \\ -y \\ z \end{vmatrix} \xrightarrow{\sigma\, xy} \begin{vmatrix} -x \\ -y \\ -z \end{vmatrix} \qquad \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

x = –3

MATRIX FOR $C_n(z)$ AXIS :

$C_n(z)$ axis, Clockwize

$$\begin{vmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

FOR C_2 AXIS :

$\theta = 180^\circ$
$\cos 180^\circ = -1$
$\sin 180^\circ = 0$

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad x = -1$$

FOR C_3 AXIS :

$\theta = 120^\circ$
$\cos 120 = -\frac{1}{2}$
$\sin 120 = \frac{\sqrt{3}}{2}$

$$\begin{vmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} & 0 \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad x = 0$$

MATRIX FOR Sn(z) AXIS :

$S_{n(z)}$ axis $= C_n$ | σ
clockwise $= C_n(z) \times \sigma$

$$\begin{vmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} = \begin{vmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

REPRESENTATION OF GROUPS

Representation is a set of matrices for a group each corresponding to a single operation in the group, that can be combine among them selves in a manner parallel to the way in which the group elements.

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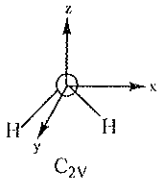
Representation

- Reducible
- Irreducible

REDUCIBLE REPRESENTATION :

Representation of higher dimension which can reduce to a lower dimension representation is known as reducible representation.
The character of identity is known as dimension.
To derive a reducible representation first of all we have to choose the basis set according to our need.

REDUCIBLE REPRESENTATION OF WATER MOLECULE



C_{2V}

Basis set = 3 cartesion coordinate

C_{2V}	E	C_2z	σ xz	σ yz
x	1	−1	1	−1
y	1	−1	−1	1
z	1	1	1	1
	3	−1	1	1

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$ ↑ identity

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$ ↑ $C_2(z)$

C_{2V}	E	C_2	σ xz	σ yz
R.R.	(3)	−1	1	1

character of identity is

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$ ↑ σxz

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$ ↑ σyz

Where R.R = Reducible Representation. This is 3D reducible representation of water molecule.

Basis Set : 9 Cartesion Coordinate :

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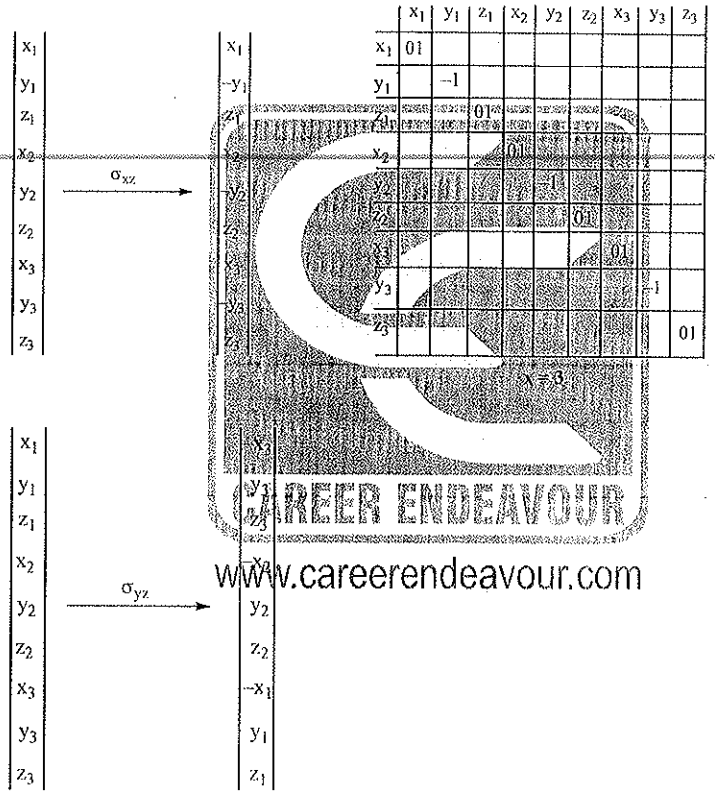
$$\begin{vmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{vmatrix} \xrightarrow{C_2(z)} \begin{vmatrix} -x_3 \\ -y_3 \\ z_3 \\ -x_2 \\ -y_2 \\ z_2 \\ -x_1 \\ -y_1 \\ z_1 \end{vmatrix}$$

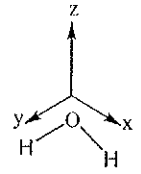
$-x_3, -y_3, z_3$ } no character contribution
$-x_2, -y_2, z_2$ } Character x = − 1 contribution
$-x_1, -y_1, z_1$ } no character contribution

0	0	0	0	0	0	0	0	−1	
0	0	0	.	.	.	.	.	.	
.	.	0	.	.	.	.	.	.	
.	.	.	−1	.	.	.	.	.	
.	.	.	.	−1	.	.	.	.	
.	.	.	.	.	1	.	.	.	
.	.	.	.	.	.	0	.	.	
.	.	.	.	.	.	.	0	.	
.	.	.	.	.	.	.	.	0	X=−1

Contribution per atom taking for only 3D:



	E	C_z	σ_{xz}	σ_{yz}
	9	−1	3	1



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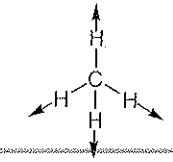
C_{2v}	E	C_2	σ_{xz}	σ_{yz}
Number of unshifted atom	3	1	3	1
contribution per atom	3	−1	1	1
R.R.	9	−1	3	1

C_4 = 1
C_3 = 0
S_4 = −1
E = 3
C_2 = −1
σ = 1
C_3 = 0
contribution per atom

TETRAHEDRAL (Td) : CH_4

basis set = bond vector



contribution per bond vector = 1 always

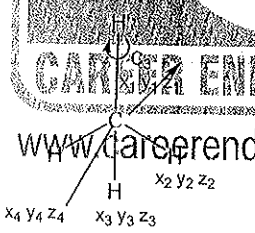
$S_4 = C_4 \times \perp \sigma$

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of unshifted vector	4	1	0	0	2
Contribution per bond vector	1	1	1	1	1
Reducible Representation (R.R.)	4	1	0	0	2

Dimension = 4

Example: CH_4

Basis set = 3 cartesion coordinate or 3N coordinate



Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of unshifted atom	5	2	1	1	3
Contribution per atom	3	0	−1	−1	1
R.R.	15	0	−1	−1	3

Dimenssion = 15

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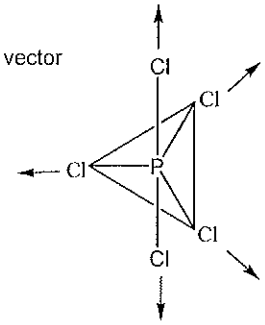
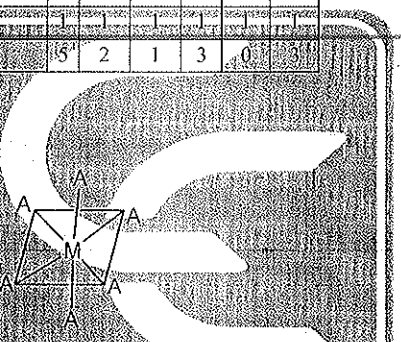
Example: $PCl_5 = D_3h$ Basis set - bond vector



Td	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_h$
Number of unshifted bond vector	5	2	1	3	0	3
Contribution	1	1	1	1	1	1
R.R.	5	2	1	3	0	3

OCTAHEDRON (Oh) :

basis set = bond vector



Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
No. of unshifted bond vector	6	0	0	2	2	0	0	0	4	2
Contribution per atom	1	1	1	1	1	1	1	1	1	1
R.R.	6	0	0	2	2	0	0	0	4	2

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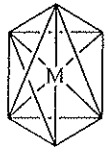
$3\ C_4 = C_4^1\ C_4^2\ C_4^3$

Same matrix



Oh :

Basis set = 3N cordinate.

Atom = 7 dimension = 3 × 7 = 21

Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$3\sigma_d$
no. of unshifted atom	7	1	1	3	3	1	1	1	5	3
Contribution per atom	3	0	–1	1	–1	–3	–1	0	1	1
R.R.	21	0	–1	3	–3	–3	–1	0	5	3

Operation	Contribution per atom
E	3
C_n	$2\cos\theta + 1$
S_n	$2\cos\theta - 1$
i	–3

$\cos 0° = 1$

$\cos 30° = \frac{\sqrt{3}}{2}$

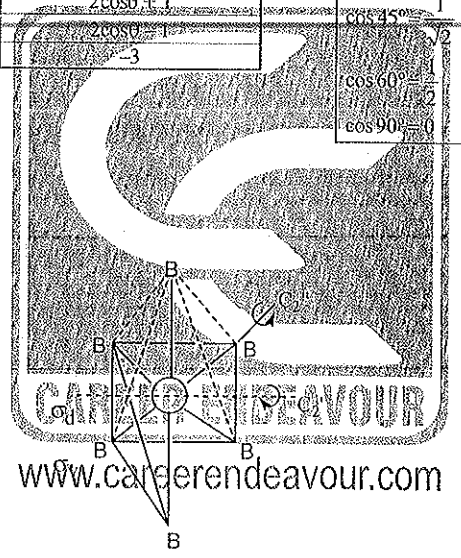
$\cos 45° = \frac{\sqrt{2}}{2}$

$\cos 60° = \frac{1}{2}$

$\cos 90° = 0$

TETRAGONAL : D_{4h}

AB_6 type molecule



Basis = bond vector

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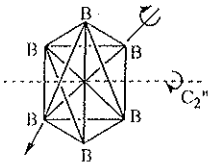
D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
No. of unshifted bond vector	6	2	2	0	2	0	0	4	4	2
Contribution perbond vector	1	1	1	1	1	1	1	1	1	1
R.R.	6	2	2	0	2	0	0	4	4	2

basis = 3 N coordinate



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Number of unshifted atom	7	3	3	3	1	1	1	5	5	3
Contribution per atom	3	1	–1	–1	–1	–3	–1	1	1	1
R.R.	21	+3	–3	–3	–1	–3	–1	5	5	3

C_n contribution $= 2\cos\theta + 1$

$n = 4\ \theta = \dfrac{360}{4} = 90^\circ\ \ C_4 = 0 + 1$

$C_4 = 1$

Where $\cos 90^\circ = 0$

S_n contribution $= 2\cos\theta - 1$

$n = 4\ \theta = 90^\circ\ \ S_4 = 2\cos 90^\circ - 1$

$S_4 = (2\times 0) - 1$

$S_4 = -1$

GROUP : A group is a collection of elements of symmetry which are interrelated according to the following rules :

(1) The products of any two elements in the group and square of each element must be an element of the same group.

e.g. In C_{2v} the elements are E, C_2, σ_{xz}, σ_{yz};

$C_2 \times C_2 = E$

$C_2 \times \sigma_{xz} = \sigma_{yz}$

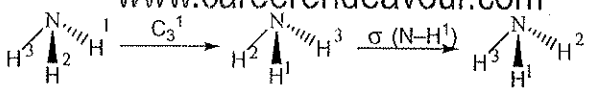
$\sigma_{xz} \times \sigma_{yz} = C_2$

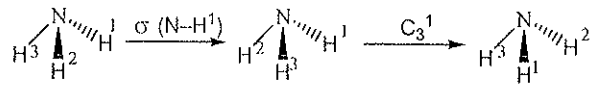
(2) In some groups the elements are commutable to each other.

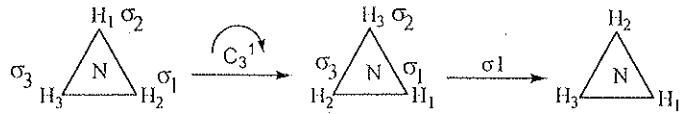
$\sigma_{xy} \times \sigma_{yz} = C_2$

e.g. C_2, $\sigma_{yz} \times \sigma_{xy} = C_2$

There groups are known as Abelian group. But in the majority of groups the elements are not cammutable. These groups are non Abelian group. e.g. C_{3v} point group.







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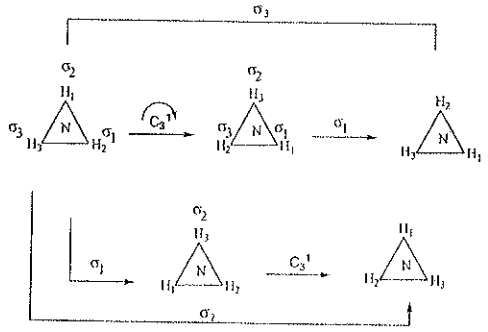

$C_3^1 \times \sigma_1 = \sigma_3$

$\sigma_1 \times C_3^1 = \sigma_2$

(3) In a group there should be an element which should be commutable with all other elements and should leave unchange. i.e. E.
The identity E is that element.

(4) For the set of elements in a group associative law of combination should be fol lowed by the elements.

$(a \times b) \times c = a \times (b \times c)$

e.g.: $(\sigma_{xz}\ \sigma_{yz})C_2 = (\sigma_{yz}\ C_2)\sigma_{xz}$

$C_2\ C_2 = \sigma_{xz}\ \sigma_{yz}$

$E = E$

(5) Each elements of a group must have its reciprocal and this should also be element of the same group.

e.g. Plane will be reciprocal of the same plane.

$\sigma_{xz} \times \sigma_{xz} = E$

$C_2 \times C_2 = E$

$C_4 \times C_4 = E$

reciprocal

$C_2 \times C_2 = E$

$C_4^1 \times C_4^3 = E$

reciprocal

$S_5^1,\ S_5^2, S_5^3,\ S_5^4 \rightarrow S_5^5$

reciprocal

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ORDER OF THE GROUP :

The number of total operations in a group is called order of group.

$C_{2v} \rightarrow E, C_2 2\sigma_v = 4$

$C_{3v} \rightarrow E, C_3^1 C_3^2, 3\sigma_v = 6$

C_n = 2n order

D_n = 4n order

Td = 24

Oh = 48

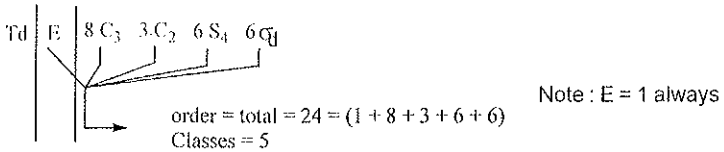
CLASSES OF THE GROUP : "A complete set of elements in a group which are conjugated to each other by similarity transfermation, are said to be in the same class."

The elements which are conjugate to each other
"The elements which are in the same class always shows the same matrix"

e.g. C_{2v} point group.

$C_{2v} = E, C_2, \sigma_{xz}, \sigma_{yz}$

In C_{2v} all 4 elements $(E, C_2, \sigma_{xz}, \sigma_{yz})$ are in the different class.



Note : E = 1 always

$Oh = E\ 8C_3, 6C_2, 6C_4, 3C_2\ (= C_4^2), i, 6S_4, 8S_6, 3\sigma_h, 6\sigma_d$

order = 1 + 8 + 6 + 6 + 3 + 1 + 6 + 8 + 3 + 6
order = 48
Classes = 10

$C_{3v} \rightarrow E \quad 2C_3 \quad 3\sigma_v$
order = 1 + 2 + 3 = 6
class = 3

GENERAL RULE FOR CLASS :

(i) Inversion(i) will be always in the seperate class if it is present.

(ii) σ_h will be always in the seperate class.

(iii) In the case of proper axis C_n^m and C_n^{n-m} will be in the same class.

C_3^1 and C_3^2
C_4^1 and C_4^3

e.g. C_8^1 and C_8^7
C_8^3 and C_8^5

(iv) There will be seperate different class for σ_d and σ_v

(v) In the case of improper axis S_n^m and S_n^{n-m} will be in the same class.

The elements which are reciprocal of each other then both lying in the same class.

IRREDUCIBLE REPRESENTATION :

A representation of lower dimension which can not be further reduce is known as irreducible representation.
The irreducible representation for a group can be derive using great orthogonality theorem (G.O.T.)

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Postulates of G.O.T. and Derivation of Irreducible representation of C_{2v} point group.

(i) Number of irreducible representation in a group are always equal to the number of classes of the group.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
IrR_1	K_1	l_1	m_1	n_1	C_{2v} class = 4
IrR_2	K_2	l_2	m_2	n_2	C_{2v} order = 4
IrR_3	K_3	l_3	m_3	n_3	
IrR_4	K_4	l_4	m_4	n_4	

Here 4 irreducible representation because C_{2v} has 4 class

(ii) The sum of square of dimension of all the irreducible representation in the group will be equal to the order of the group.
The character related to identity known as dimension according to Rule (ii)

$k_1^2 + k_2^2 + k_3^2 + k_4^2 = 4$

$l^2 + l^2 + l^2 + l^2 = 4$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
IrR_1	1	ℓ	m_1	n_1
IrR_2	1	ℓ_2	m_2	n_2
IrR_3	1	ℓ_3	m_3	n_3
IrR_4	1	ℓ_4	m_4	n_4
	dimension = 1			

(iii) The sum of squares of the characters of an irreducible representation will be equal to the order of group.
i.e.

$1^2 + \ell_2^2 + m_2^2 + n_2^2 = 4$
$1^2 + \ell_3^2 + m_3^2 + n_3^2 = 4$
$1^2 + \ell_4^2 + m_4^2 + n_4^2 = 4$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
IrR_1	1	1	1	1
IrR_2	1	ℓ_2	m_2	n_2
IrR_3	1	ℓ_3	m_3	n_3
IrR_4	1	ℓ_4	m_4	n_4

$1^2 + 1^2 + 1^2 + 1^2 = 4$

(iv) The characters of any 2 irreducible representation in the same group will be always orthogonal to each other i.e. on multiply any 2 Irreducible representation the result should be 0.

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C_{2v}	E	C_2	σ_{xz}	σ_{yz}
IrR_1	1	1	1	1
IrR_2	1	1	−1	−1
IrR_3	1	ℓ_3	m_3	n_3
IrR_4	1	ℓ_4	m_4	n_4

$1\times1+1\times\ell_2+1\times m_2+1\times n_2=0$

$\ell_2=1, m_2=-1, n_2=-1$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
IrR_1	1	1	1	1
IrR_2	1	1	−1	−1
IrR_3	1	−1	1	−1
IrR_4	1	−1	−1	1

$IrR_2\times IrR_3=O$

$=1\times1+1\times-1+-1\times1+-1\times-1$

$=1\quad -1\quad -1\quad +\quad 1$

$=0$

e.g. C_{3v}

Rule : (1)

C_{2v}	E	$2C_3$	$3\sigma_v$	order = 6
IrR_1	1	ℓ_1	m_1	classes = 3
IrR_2	1	ℓ_2	m_2	
IrR_3	2	ℓ_3	m_3	

Rule : (2) $k_1^2+k_2^2+k_3^2=6$

$1^2+1^2+2^2=6$

C_{3v}	E	$2C_3$	$3\sigma_v$

Rule : (3) $1^2+2\times\ell_1^2+3\times m_1^2=6$

$1^2+2\times1^2+3\times1^2=6$

Rule : (4) $IR_1\times IR_2=0$

$1\times1+2(1\times\ell_2)+3(1\times m_2)=0$

$IR_1\times IR_3=0$

$IR_2\times IR_3=0$

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Rule : (1) $IR_1\times IR_3=0$

$=1\times2+2(1\times\ell_3)+3(1\times m_3)=0$

$=IR_1+IR_3=2+2\ell_3+3m_3=0$ .....(I)

C_3v	E	$2C_3$	$3\sigma_v$
IR_1	1	1	1
IR_2	1	1	−1
IR_3	2	ℓ_3	m_3

$IR_2\times IR_3=0$

$=1\times2+2(1\times\ell_3)+3(-1\times m_3)=0$

$IR_2\times IR_3=2+2\ell_3-3m_3=0$ .....(2)

$\ell_3=-1$

$m_3=0$

on addition

$2\ell_3+3m_3=-2$.....(I)

$2\ell_3-3m_3=-2$.....(2)

$4\ell_3=-4$

$\ell_3=\frac{-4}{4}=-1$ $\boxed{\ell_3=-1}$

Put ℓ_3 value in eq. (1) then

$2\times-1+3m_3=-2$

$-2+3m_3=-2$

$3m_3=-2+2$

$m_3=0$

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CHARACTER TABLE AND ITS DERIVATION

A character table is a way which can be utilised for application of group theory for the molecular symmetry.

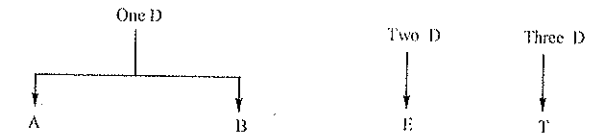
Each character table has 4 columns and different symbols in them which can be explain by taking example of C_{2v} point group.

COLUMN– I :

I[st] column of character table shows mulliken symbol for irreducible representation of the group.

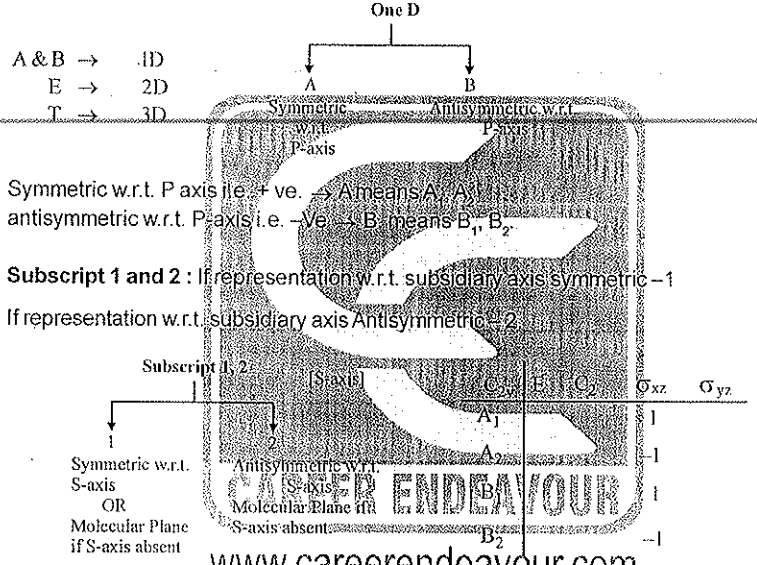
A,B,E & T : The mulliken symbol can be decided by the following rule.

Character table have
- A, B, E, T
- 1, 2, – subscript
- u, g, – subscript
- I, II – supercript



C_{2v}	E	C_2	σ_{xz}	σ_{yz}
IR_1	1	1	1	1
IR_2	1	1	−1	−1
IR_3	1	−1	1	−1
IrR_4	1	−1	−1	1

If dimension 1 then put A or B
If dimension 2 then put E
If dimension 3 then put T
Alphabet A, B, E & T are notation for dimension of irreducible representation.



Symmetric w.r.t. P axis i.e. +ve. → A means A_1, A_2
antisymmetric w.r.t. P-axis i.e. −ve. → B means B_1, B_2

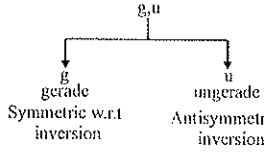
Subscript 1 and 2 : If representation w.r.t. subsidiary axis symmetric – 1

If representation w.r.t. subsidiary axis Antisymmetric – 2

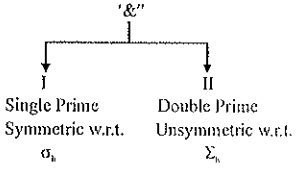
Subscript 1, 2
1
2
Symmetric w.r.t. S-axis OR Molecular Plane if S-axis absent
Antisymmetric w.r.t. S-axis Molecular Plane if S-axis absent

	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

Subscript g, u :



Superscript ' & " :



e.g. : C_{3v}

C_{2v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

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Q. What is the meaning of E'_g mulliken symbol?

Ans. This is 2 dimensional irreducible representation which is Antisymmetric w.r.t. P-axis
Symmetric w.r.t. inversion
Symmetric w.r.t. σ_h in the molecule.

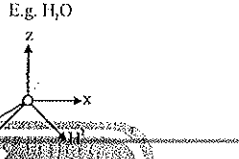
Column II :

IInd column of charater table shows irreducible representation of the groups which can be derive using G.O.T.

Column III :

IIIrd column explain transformation properties of 3-cartesion coordinate x,y, z and 3 rotational axis i.e. R_x, R_y, R_z.

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
x	1	−1	1	−1	B_1
y	1	−1	−1	1	B_2
z	1	1	1	1	A_1
R_x	1	−1	−1	1	B_2
R_y	1	−1	1	−1	B_1
R_z	1	+1	−1	−1	A_2



Column IV :

IVth column explain transformation properties of quadratic functions of cartision coordinates like transformation properties of x^2, y^2, z^2.

$x^2 - y^2$, xy, yz, xz, $x^2 - y^2 - z^2$

C_{2v}	E	C_2	σ_{xz}	σ_{yz}	
x	1	−1	1	−1	
y	0	−1	−1	1	
z	1	1	1	1	
x^2, y^2, z^2	0	1	1	1	A_1
xz	1	−1	1	−1	B_1
yz	1	−1	−1	1	B_2
xy	1	1	−1	−1	A_2

C_{2v}	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

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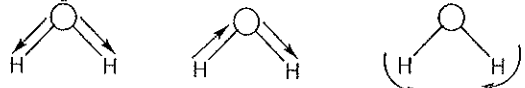
Example: H_2O :



C_2 ✓ σ_{xz} σ_{yz} ✓ → A_1 vibration

C_2 × σ_{xz} ✓ σ_{yz} × → B_1 vibration

C_2 ✓ σ_{xz} ✓ σ_{yz} ✓ → A_1 vibration

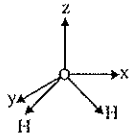
RELATION BETWEEN REDUC-

A_1 & B_1 vibrations are I.R. active.

IBLE AND IRREDUCIBLE REPRESENTATION

Reduction of a reducible representation : conversion of a higher dimension to a lower dimension representation.

C_{2v}	E	C_2	σ_{xy}	σ_{yz}
R.R.	9	−1	3	1



C_{2v}	E	C_2	σ_{xy}	σ_{yz}
A_1	1	1	1	1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1

Q. How many times A_1 comes given by the formula?

$$n_{A_1} = \frac{1}{4}(9\times1 + -1\times1 + 3\times1 + 1\times1)$$
$$n_{A_1} = \frac{1}{4}(9-1+3+1)$$
$$n_{A_1} = \frac{12}{4}$$
$$n_{A_1} = 3$$

Check : Number comes always a complete no.

$$n_{A_2} = \frac{1}{4}(9\times1 + -1\times1 + 3\times1 + 1\times-1)$$
$$n_{A_2} = \frac{1}{4}(9-1-3-1)$$
$$n_{A_2} = \frac{4}{4} = 1$$
$$n_{A_2} = 1$$

$$n_{B_1} = \frac{1}{4}(9\times1 + -1\times-1 + 3\times1 + 1\times-1)$$
$$= \frac{1}{4}(9+1+3-1)$$
$$= \frac{12}{4} = 3$$
$$n_{B_1} = 3$$

$$n_{B_2} = \frac{1}{4}(9\times1 + -1\times-1 + -1\times3 + 1\times1)$$
$$n_{B_2} = \frac{1}{4}(9+1-3+1)$$
$$n_{B_2} = 2$$

then $\boxed{3A_1 + 1A_2 + 3B_1 + 2B_2}$

it is count the dimension = 9

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CHARACTER OF IDENTITY IN τ_r :

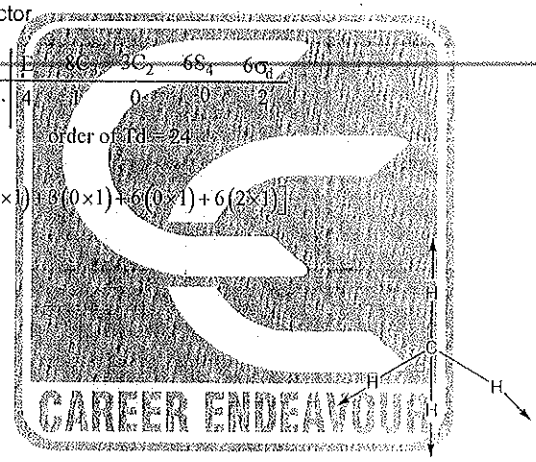
A_1	1	1	1	1
A_1	1	1	1	1
A_1	1	1	1	1
A_2	1	1	−1	−1
A_2	1	1	−1	−1
B_1	1	−1	1	−1
B_1	1	−1	1	−1
B_1	1	−1	1	−1
B_2	1	−1	−1	1
B_2	1	−1	−1	1
Total	9	−1	3	1

Tetrahedron (Td) : CH_4

Basis set : bond vector

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
R.R.	4	1	0	0	2

order of Td = 24



$$n_{A_1} = \frac{1}{24}\left[4\times1 + 8(1\times1) + 3(0\times1) + 6(0\times1) + 6(2\times1)\right]$$
$$= \frac{1}{24}(4+8+12)$$
$$= \frac{24}{24}$$
$$n_{A_1} = 1$$

$$n_{A_1} = 1$$

$$n_{A_2} = \frac{1}{24}\left[(4\times1 + 8(1\times1) + 3(0\times1) + 6(0\times-1) + 6(2\times-1))\right]$$

$$n_{A_2} = \frac{1}{24}(4+8+0+0-12)$$
$$n_{A_2} = \frac{0}{24}$$
$$n_{A_2} = 0$$

$$n_E = \frac{1}{24}\left[(4\times2) + 8(1\times-1) + 3(0\times2) + 6(0\times0) + 6(2\times0)\right]$$
$$n_E = \frac{1}{24}(8-8+0+0+0)$$
$$n_E = \frac{0}{24}$$
$$n_E = 0$$

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$$n_{T_1} = \frac{1}{24}\left[(4\times3)+8(1\times0)+3(0\times-1)+6(0\times+1)+6(2\times-1)\right]$$
$$n_{T_1} = \frac{1}{24}(12+0+0+0-12)$$
$$n_{T_1} = \frac{0}{24}$$
$$n_{T_1} = 0$$

$$n_{T_2} = \frac{1}{24}\left[4\times3+8(1\times0)+3(0\times-1)+6(0\times-1)+6(2\times1)\right]$$
$$n_{T_2} = \frac{1}{24}(12+0+0+0+12)$$
$$n_{T_2} = \frac{24}{24}=1$$
$$n_{T_2} = 1$$

So $A_1 + T_1$

For Recheck :

A_1	1	1	1	1	1
T_1	1	1	−1	1	−1
R.R.	1	1	0	1	0
Total	4	2	0	2	0

D_{3h} :

BF_3 basis set = 5N coordinate

order = 12

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$3S_3$	$3\sigma_v$
No. unshifted atom	4	1	0	4	1	2
contribution per atom	3	0	−1	3	0	1
R.R.	12	0	−2	4	−2	2

$$n_{A_1}' = \frac{1}{2}\left(12\times1+2(0\times1)+3(-2\times1)+(4\times1)+2(-2\times1)+3(2\times1)\right)$$
$$n_{A_1}' = \frac{1}{2}(12+0-\beta+\alpha-\alpha+\beta)$$
$$n_{A_1}' = \frac{12}{12}=1$$
$$n_{A_1}' = 1$$

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$$n_{A_2}' = \frac{1}{12}\left[(12\times1+2(0\times1)+3(-2\times-1)+(4\times1)+2(-2\times1)+3(2\times-1)\right]$$
$$n_{A_2}' = \frac{1}{12}(12+0+\beta+\alpha-\alpha-\beta)$$
$$n_{A_2'=\frac{12}{12}=1}$$
$$n_{A_2}' = 1$$

$$nE' = \frac{1}{12}\left[(12\times2)+2(0\times-1)+3(-2\times0)+(4\times2)+2(-2\times-1)+3(2\times0)\right]$$
$$nE' = \frac{1}{12}(24+0+0+8+4+6)$$
$$nE' = \frac{36}{12}=3$$
$$nE' = 3$$

$$n_{A_1}'' = \frac{1}{12}\left[(12\times1+2(0\times1)+3(-2\times1)+(4\times-1)+2(-2\times-1)+3(2\times-1)\right]$$
$$n_{A_1}'' = \frac{1}{12}(12+0-6-4+4-6)$$
$$n_{A_1}'' = \frac{0}{12}$$
$$n_{A_1}'' = 0$$

$$n_{A_2}'' = \frac{1}{12}\left[(12\times1+2(0\times1)+3(-2\times-1)+(4\times-1)+2(-2\times-1)+3(2\times1)\right]$$
$$n_{A_2}'' = \frac{1}{12}(12+0+6-4+4+6)$$
$$n_{A_2}'' = \frac{24}{12}=2$$
$$n_{A_2}'' = 2$$

$$nE'' = \frac{1}{12}\left[(12\times2+2(0\times-1)+3(-2\times0)+(4\times-2)+2(-2\times1)+3(2\times0)\right]$$
$$nE'' = \frac{1}{12}(24+0+0-8-4+0)$$
$$nE'' = \frac{12}{12}=1$$
$$nE'' = 1$$

So total $= 1\times A_1' + 1\times A_2' + 3\times E' + 0\times A_1'' + 2\times A_2'' + 1\times E''$

Rep. $= A_1' + A_2' + 3E' + 0 + 2A_2'' + E''$

Irreducible representation = $\boxed{A_1' + A_2' + 3E' + 2A_2'' + E''}$

Q.

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
R.R.	15	0	−1	−1	3

order = 24

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$$n_{A_1} = \frac{1}{24}\left[15\times1+8(0\times1)+3(-1\times1)+6(-1\times1)+6(3\times1)\right]$$
$$n_{A_1} = \frac{1}{24}(15+0-3-6+18)$$
$$n_{A_1} = \frac{24}{24} = 1$$
$$n_{A_1} = 1$$

$$nA_2 = \frac{1}{24}\left[15\times1+8(0\times1)+3(-1\times1)+6(-1\times-1)+6(+3\times-1)\right]$$
$$nA_2 = \frac{1}{24}(15+0-3+6-18)$$
$$nA_2 = \frac{1}{24}(12-12) = \frac{0}{24}$$
$$nA_2 = 0$$

$$nE = \frac{1}{24}\left[15\times2+8(0\times-1)+3(-1\times2)+6(-1\times0)+6(3\times0)\right]$$
$$nE = \frac{1}{24}(30+0-6+0+0)$$
$$nE = \frac{24}{24} = 1$$
$$nE = 1$$

$$nT_1 = \frac{1}{24}(15\times3+8(0\times0)+3(-1\times-1)+6(-1\times1)+6(3\times-1)$$
$$nT_1 = \frac{1}{24}(45+0+3-6-18)$$
$$nT_1 = \frac{1}{24} = (48-24)$$
$$nT_1 = \frac{24}{24} = 1$$
$$nT_1 = 1$$

$$nT_2 = \frac{1}{24}(15\times3+8(0\times0)+3(-1\times-1)+6(-1\times-1)+6(3\times-1)$$
$$nT_2 = \frac{1}{24}(45+0+3+6+18)$$
$$nT_2 = \frac{72}{24} = 3$$
$$nT_2 = 3$$

So total $\rightarrow 1\times A_1+0\times A_2+1\times E+1\times T_1+3\times T_2$
$\rightarrow A_1+0+E+T_1+3T_2$

irreducible representation $\Rightarrow$ $\boxed{A_1+E+T_1+3T_2}$

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For Cheking :

A_1	1	1	1	1	1
E	2	−1	2	0	0
T_1	3	0	−1	1	−1
T_2	3	0	−1	−1	1
T_2	3	0	−1	−1	1
T_2	3	0	−1	−1	1
Total R.R.	15	0	−1	−1	3

Note : The element which having its IIIrd & IVth column is empty then that element having not any value means 0 value.

In Td $nA_2 = 0$

i.e. In D_{3h} $nA_1'' = 0$

Q.

C_{2h}	E	C_2	i	σ_h	order = 4
R.R.	12	0	0	4	

$$nA_g = \frac{1}{4}(12\times1+0\times1+0\times1+4\times1)$$
$$nA_g = \frac{1}{4}(12+0+0+4)$$
$$nA_g = \frac{16}{4} = 4$$
$$nA_g = 4$$

$$nB_g = \frac{1}{4}\left[(12\times1+0\times-1+0\times1+4\times-1)\right]$$
$$nB_g = \frac{1}{4}(12+0+0-4)$$
$$nB_g = \frac{8}{4} = 2$$
$$nB_g = 2$$

$$nA_u = \frac{1}{4}\left[(12\times1+0\times1+(0\times-1)+(4\times-1)\right]$$
$$nA_u = \frac{1}{4}(12+0+0-4)$$
$$nA_u = \frac{8}{4} = 2$$
$$nA_u = 2$$

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$$nB_u = \frac{1}{4}\left[(12\times1+0\times-1+0\times-1+4\times1)\right]$$

$$nB_u = \frac{1}{4}(12+0+0+4)$$

$$nB_u = \frac{16}{4} = 4$$

$$nB_u = 4$$

Total irreducible representation $= 4\times A_g + 2\times B_g + 2\times A_u + 4\times B_u$

$$\text{Irr Rep.} = \boxed{4A_g + 2B_g + 2A_u + 4B_u}$$

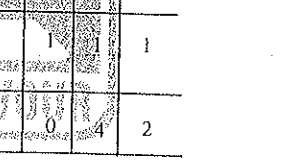
For Checking:

A_g	1	1	1	1
A_g	1	1	1	1
A_g	1	1	1	1
A_g	1	1	1	1
B_g	1	−1	1	−1
B_g	1	−1	1	−1
A_u	1	1	−1	−1
A_u	1	1	−1	−1
B_u	1	−1	−1	1
B_u	1	−1	−1	1
B_u	1	−1	−1	1
B_u	1	−1	1	1
R.R.	12	0	0	4

Q.

C_{3v}	E	$2C_3$	$3\sigma_v$
Number unshifted atom	4	1	2
contribution per atom	3	0	1
R.R.	12	0	2

basis set → 3N coordinate



C_3V

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C_n order $= 2n$, $C_3v = 2\times3 = 6$

order $= 6$

$$n\,A_1 = \frac{1}{6}\left[(12\times1+0\times1+3(2\times1))\right] = \frac{1}{6}(12+6) = \frac{18}{6} = 3$$

$$n\,A_1 = 3$$

$$nA_2 = \frac{1}{6}\left[(12\times1+3\times2-1)\right] = \frac{1}{6}(12-6) = \frac{6}{6} = 1$$

$$nA_2 = 1$$

$$nE = \frac{1}{6}(12\times2+0+0) = \frac{24}{6} = 4$$

$$nE = 4$$

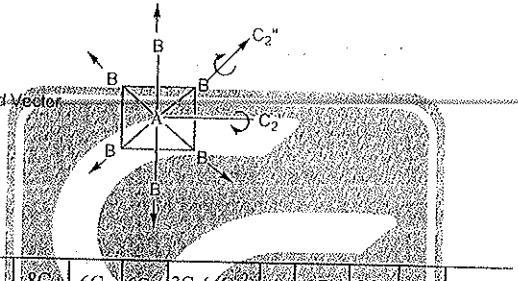
total irreducible representation $= 3\times A_1 + 1\times A_2 + 4\times E$

Total irreducible representation $= 3A_1 + A_2 + 4E$

For Checking :

A_1	1	1	1
A_1	1	1	1
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0
E	2	−1	0
E	2	−1	0
E	2	−1	0
Total	12	0	2

Q. Derive reducible representation for Oh(Octahedron)



Basis set = Bond Vector

Order = 48

Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
No. of unshifted bond	6	0	0	2	2	0	0	0	4	2
Contribution per bond vector	1	1	1	1	1	1	1	1	1	1
R.R.	6	0	0	2	2	0	0	0	4	2

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$$nA_{1g} = \frac{1}{48}\left[(6\times1+8\times0\times1+6\times0\times1+6\times2\times1+3\times2\times1+\times1+0\times0\times1+8\times0\times1+3\times4\times1+6\times2\times1)\right]$$

$$nA_{1g} = \frac{1}{48}(6+0+0+12+6+0+0+0+12+12)$$

$$nA_{1g} = \frac{48}{48} = 1$$

$$nA_{2g} = \frac{1}{48}\left[(6\times1+8\times0\times1+6\times(0\times-1)+6\times(2\times-1)+3\times2\times1+0\times1+6\times(0\times-1)+8\times0\times1+3\times4\times1+6\times(2\times-1)\right]$$

$$nA_{2g} = \frac{1}{48}(6+0+0-12+6+0+0+0+12-12)$$

$$nA_{2g} = \frac{1}{48}(12-12+12-12) = \frac{0}{48} = 0 \qquad nA_{2g} = 0$$

$$nE_g = \frac{1}{48}\left[(6\times2+8\times(0\times-1)+6\times0\times0+6\times2\times0+3\times2\times2+0\times2+6\times0\times0+8\times0)(0\times-1)3\times4\times2+6\times2\times0\right]$$

$$nE_g = \frac{1}{48}(12+0+0+0+12+0+0+0+24+0)$$

$$nE_g = \frac{1}{48} = (12+12+24) = \frac{48}{48} = 1$$

$$\boxed{nE_g = 1}$$

$$nT_{1g} = \frac{1}{48}\left[(6\times3+8\times0\times0+6\times(0\times-1)+6\times2\times1+3\times(2\times-1)+0\times3+6\times0\times1+8\times0\times0+3\times(4\times-1)+6\times(2\times-1)\right]$$

$$nT_{1g} = \frac{1}{48}(18+0+0+12-6+0+0+0-12-12)$$

$$nT_{1g} = \frac{1}{48} = (24-24) = \frac{0}{48} = 0$$

$$\boxed{nT_{1g} = 0}$$

$$nT_{2g} = \frac{1}{48}\left[(6\times3+8\times0\times0+6\times0\times1+6\times(2\times-1)+3\times(2\times-1)+1\times0\times3+6\times(0\times-1)+8\times0\times0+3\times(4-1)+6\times2\times1)\right]$$

$$nT_{2g} = \frac{1}{48}(18+0+0-12-6+0+0+0-12+12)$$

$$nT_{2g} = \frac{1}{48} = (18-18) = \frac{0}{48} = 0$$

$$\boxed{nT_{2g} = 0}$$

$$nA_{1u} = \frac{1}{48}\left[(6\times1+8\times0\times1+6\times0\times1+6\times2\times1+3\times2\times1+1\times(0\times-1)+6\times(0\times-1)+8\times(0\times-1)+3\times(4\times-1)+6\times(2\times-1)\right]$$

$$nA_{1u} = \frac{1}{48}(6+0+0+12+6+0+0+0-12-12)$$

$$nA_{1u} = \frac{0}{48} = 0$$

$$\boxed{nA_{1u} = 0}$$

$$nA_{2u} = \frac{1}{48}\left[(6\times1+8\times0\times1+6\times(0\times-1)+6\times(2\times-1)+3\times2\times1+1\times(0\times-1)+6\times0\times1+8\times(0\times-1)+3\times(4\times-1)+6\times2\times1)\right]$$

$$nA_{2u} = \frac{1}{48}(6+0+0-12+6+0+0+0-12+12)$$

$$nA_{2u} = \frac{0}{48} = 0$$

$$\boxed{nA_{2u} = 0}$$

$$nE_u = \frac{1}{48}\left[(6\times2+8\times(0\times-1)+6\times0\times0+6\times2\times0+3\times2\times2+1\times(0\times-2)+6\times0\times0+8\times0\times1+3\times(4\times-2)+6\times2\times0)\right]$$

$$nE_u = \frac{1}{48}(12+0+0+0+12+0+0+0-24+0)$$

$$nE_u = \frac{0}{48} = 0 \qquad \Rightarrow \boxed{nE_u = 0}$$

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$$nT_{1u} = \frac{1}{48}\left[(6\times3+8\times0\times0+6\times(0\times-1)+6\times2\times1+3\times(2\times-1)+1\times(0\times-3)+6\times(0\times-1)+8\times0\times0+3\times4\times1+6\times2\times1)\right]$$

$$nT_{1u} = \frac{1}{48}(18+0+0+12-6+0+0+0+12+12)$$

$$nT_{1u} = \frac{48}{48} = 1$$

$$\boxed{nT_{1u} = 1}$$

$$nT_{2u} = \frac{1}{48}\left[(6\times3+8\times0\times0+6\times0\times1+6\times2\times-1+3\times2\times-1+1\times0\times-3+6\times0\times1+8\times0\times0+3\times4\times1+6\times2\times-1)\right]$$

$$nT_{2u} = \frac{1}{48}(18+0+0-12-6+0+0+0+12-12)$$

$$nT_{2u} = \frac{0}{48} = 0$$

$$\boxed{nT_{2u} = 0}$$

Total irreducible representation

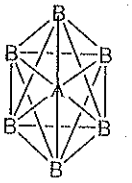
$$= 1\times A_{1g} + 0\times A_{2g} + 1\times E_g + 0\times T_{1g} + 0\times T_{2u} + 0\times A_{1u} + 0\times A_{2u} + 0\times E_u + 1\times T_{1u} + 0\times T_{2u}$$

$$\text{I.R.} = A_{1g} + 0 + E_g + 0 + 0 + 0 + 0 + 0 + T_{1u}$$

$$\boxed{\text{R.R.} = A_{1g} + E_g + T_{1u}}$$

For Checking :

A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
E_g	2	−1	0	0	−2	2	0	−1	−2	0	1	1	−1	−2	2	0	−1	1	0	0	−2	2	0	−1
T_{1u}	3	0	1	−1	1	1	0	0	−1	−1	1	−1	0	1	−1	−1	0	0	1	−1	1	1	0	0
R.R.	6	0	2	−2	0	4	0	0	−4	0	3	1	−1	−1	1	−1	−1	1	1	−1	−1	4	0	0



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OCTAHEDRON (Oh) :

basis set - 3N coordinate

Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
No. of unshifted atom	7	1	1	3	3	1	1	1	5	3
Contribution per atom	3	0	−1	1	−1	−3	−1	0	1	1
R.R.	21	0	−1	3	−3	−3	−1	0	5	3

Order = 48

$$nA_{1g} = \frac{1}{48}\left[(21\times1)+8(0\times1)+6(-1\times1)+6(3\times1)+3(-3\times1)+1(-3\times1)+6(-1\times1)+8(0\times1)+3(5\times1)+6(3\times1)\right]$$

$$nA_{1g} = \frac{1}{48}\left[21+0-6+18-9-3-6+0+15+18\right]$$

$$nA_{1g} = \frac{1}{48}(21+15+18-6)$$

$$nA_{1g} = \frac{1}{48}(21+15+12)$$

$$nA_{1g} = \frac{48}{48} = 1$$

$$\boxed{nA_{1g} = 1}$$

$nA_2 = 0$ because not having value in III & IV column

$$nE_g = \frac{1}{48}\left[(21\times2+3\times(-3\times2)+1-3\times2+3\times5\times2)\right]$$

$$nE_g = \frac{1}{48}(42-18-6+30)$$

$$= \frac{1}{48}(-24+72)$$

$$E_g = \frac{48}{48} = 1$$

$$\boxed{nE_g = 1}$$

$$nT_{1g} = \frac{1}{48}\left[(21\times3+0+(6\times-1\times-1)+6\times3\times1+3\times(-3\times-1)+1\times(-3\times3)+6\times(-1\times1)+0+3\times(5-1)+6\times(3\times-1)\right]$$

$$nT_{1g} = \frac{1}{48}(63+6+18+9-6+0-15-18)$$

$$nT_{1g} = \frac{1}{48}(96-48)$$

$$nT_{1g} = \frac{1}{48}$$

$$nT_{1g} = \frac{48}{48} = 1$$

$$\boxed{nT_{1g} = 1}$$

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$$nT_{2g} = \frac{1}{48}\left[(63+(6\times-1)+6\times(3\times-1)+3\times(-3\times-1)+1\times(-3\times3)+6\times(-1\times-1)+(3\times5-1)+6\times3\times1\right]$$

$$nT_{2g} = \frac{1}{48}(63-6-18+9-9+6-15+18)$$

$$nT_{2g} = \frac{1}{48}(72-36)$$

$$nT_{2g} = \frac{48}{48} = 1$$

$$\boxed{nT_{2g} = 1}$$

$$nT_{1u} = \frac{1}{48}\left[(21\times3+6\times(-1\times-1)+6\times3\times1+3\times(-3\times-1)+1\times(-3\times-3)+6\times(-1\times-1)+3\times51+6\times3\times1)\right]$$

$$nT_{1u} = \frac{1}{48}(63+6+18+9+9+6+15+18)$$

$$nT_{1u} = \frac{144}{48} = 3$$

$$\boxed{nT_{1u} = 3}$$

$$\text{Total} = 1\times A_{1g} + 1\times E_g + 1\times T_{1g} + 1\times T_{2g} + 3\times T_{1u} + T_{2u}$$

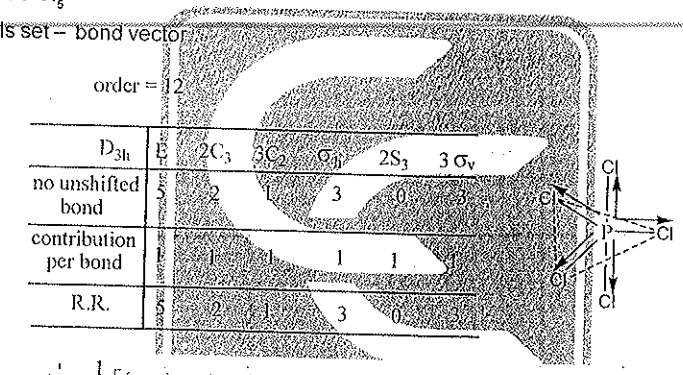
$$\text{Total I.R.} = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}$$

$$\boxed{\text{Total R.R.} = A_{1g} + E_g + T_{1g} + T_{2g} + 3T_{1u} + T_{2u}}$$

D_{3h} :

e.g. : PCl_5

basis set – bond vector



order = 12						
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
no unshifted bond	5	2	1	3	0	3
contribution per bond	1	1	−1	1	1	−1
R.R.	5	2	−1	3	0	−3

$$nA_1' = \frac{1}{12}\left[(5\times1)+2(2\times1)+3(1\times1)+1(3\times1)+2(0\times1)+3(3\times-1)\right]$$

$$nA_1' = \frac{1}{12}\left[5+4+3+3+9\right]$$

$$\boxed{nA_1' = 2}$$

$$nA_2' = \frac{1}{12}\left[(5\times1)+2(2\times1)+3(1\times-1)+1(3\times-1)+2(0\times1)+3(3\times-1)\right]$$

$$nA_2' = \frac{1}{12}\left[5+4-3+3-9\right]$$

$$\boxed{nA_2' = 0}$$

$$nE' = \frac{1}{12}\left[(5\times2)+2(2\times-1)+3(1\times0)+1(3\times2)+2(0\times-1)+3(3\times0)\right]$$

$$nE' = \frac{1}{12}\left[10-4+6\right]$$

$$\boxed{nE' = 1}$$

$$nA_1'' = \frac{1}{12}\left[(5\times1)+2(2\times1)+3(1\times1)+1(3\times-1)+2(0\times-1)+3(3\times-1)\right]$$

$$nA_1'' = \frac{1}{12}[5+4+3-3-9]$$

$$\boxed{nA_1'' = 0}$$

$$nA_2'' = \frac{1}{12}\left[(5\times1)+2(2\times1)+3(1\times-1)+1(3\times-1)+2(0\times-1)+3(3\times1)\right]$$

$$nA_2'' = \frac{1}{12}[5+4-3-3+9]$$

$$\boxed{nA_2'' = 1}$$

$$nE'' = \frac{1}{12}\left[(5\times2)+2(2\times-1)+3(1\times0)+1(3\times-2)+2(0\times1)+3(3\times0)\right]$$

$$nE'' = \frac{1}{12}[10-4-6]$$

$$\boxed{nE'' = 0}$$

$$\boxed{\text{Total} = 2A_1' + E' + A_2''}$$

For Checking :

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1'	1	1	1	1	1
A_1''	1	1	1	−1	−1
E'	2	−1	2	0	0
E''	2	−1	−2	0	0
Total	5	2	1	3	0	3

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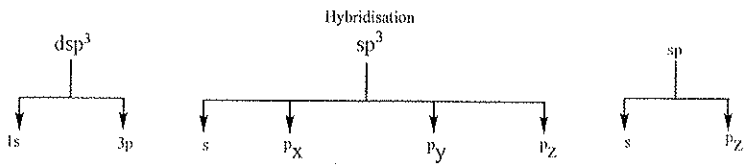
EXPLANATION OF HYBRIDIZATION (BONDING)

AB_n TYPE MOLECULE :



Q. The character table of Tetrahedron (Td) is given below. Answer the following questions

(i) What is the order of group?
(ii) What is the number of classes in the group?
(iii) What is the number of irreducible representation in the group?
(iv) Prove that irreducible representation A_1 & E are orthogonal to each other
(v) Find out the value of direct product
$A_1 \times E$
$E \times E$
(vi) Consider a AB_4 type Tetrahedral molecule with s, p & d-orbitals on the central atom. and find out the combinations of orbitals for σ bonding.
(vii) Explain the best fit combination of orbitals for CH_4 & MnO_4^{-2}.

Ans. (i) order of group = 24
(ii) no. of classes in the group = 5
(iii) irreducible representation always equal to the no. of classes present in the group = 5
(iv) Proof of irreducible representation of $A_1 \times E$ are orthogonal to each other

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	value from character table
A_1	1	1	1	1	1	
E	2	−1	2	0	0	

$$A_1 \times E = \left[1\times2+8(1\times-1)+3(1\times2)+6(1\times0)+6(1\times0)\right]$$
$$= 2-8+6 = 0$$

So the irreducible representation of A_1 & E are orthogonal to each other.

(v) The direct product

$$A_1 \times E = \frac{E \quad 8C_3 \quad 3C_2 \quad 6S_4 \quad 6\sigma_d}{2 \quad -1 \quad 2 \quad 0 \quad 0}$$

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Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	
A_1	1	1	1	1	1	
E	2	−1	2	0	0	
Direct Product $A_1 \times E$	2	−1	2	0	0	✓ R.R.
$E \times E$	4	1	4	0	0	✓ R.R.

For $E \times E$

$$nA_1 = \frac{1}{24}\left[(4\times1)+8(1\times1)+3(4\times1)+6(0\times1)+6(0\times1)\right]$$

$$nA_1 = \frac{1}{24}[4+8+12] = \frac{24}{24} = 1$$

$$nA_2 = \frac{1}{24}\left[(4\times1)+8(1\times1)+3(4\times1)+6(0\times-1)+6(0\times-1)\right]$$

$$nA_2 = \frac{1}{24}[4+8+12] = 1$$

$$nE = \frac{1}{24}[(4\times2)+8(1\times-1)+3(4\times2)+6(0\times0)+6(0\times0)]$$

$$nE = \frac{1}{24}[8-8+24]$$

$$nE = 1$$

$$nT_1 = \frac{1}{24}[(4\times3)+(1\times0)+3(4\times-1)]$$

$$nT_1 = \frac{1}{24}[(12-12)] = \frac{0}{24} = 0$$

$$nT_2 = \frac{1}{24}[(4\times3)+8(1\times0)+3(4\times-1)] = \frac{1}{24}[12-12] = 0$$

Total R.R for $E\times E = A_1 + A_2 + E$.

For $A_1 \times E$:

	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
R.R	2	−1	2	0	0
$A_1\times E$					

$$nA_1 = \frac{1}{24}[(2\times1)+8(-1\times1)+3(2\times1)] = 0$$

$$nA_2 = \frac{1}{24}[(2\times1)+8(-1\times1)+3(2\times1)] = 0$$

$$nE = \frac{1}{24}[(2\times2)+8(-1\times-1)+3(2\times2)]$$

$$nE = \frac{1}{24}(4+8+12) = \frac{24}{24} = 1$$

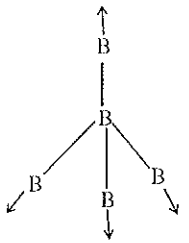
$$nT_1 = \frac{1}{24}[(2\times3)+8(-1\times0)+3(2\times-1)] = \frac{1}{24}(6-6) = 0$$

$$nT_2 = \frac{1}{24}[(2\times3)+8(-1\times0)+3(2\times-1)] = 0$$

Total R.R. for $A_1E = E$

(vi) **Step (i)** Derive reducible representation using bond vectors as basis.
Step (ii) Reduce the R. R. obtained.
Step (iii) Find out the transformation properties of orbitals according to mulliken symbols.
Step (iv) Make the combinations.

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
	4	1	0	0	2
	1	1	1	1	1
R.R	4	1	0	0	2



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$$nA_1 = \frac{1}{24}[(4\times1)+8(1\times1)+6(2\times1)]$$

$$nA_1 = \frac{1}{24}(4+8+12)$$

$$nA_1 = \frac{24}{25} = 1$$

$$nA_2 = \frac{1}{24}[(4\times1)+8(1\times1)+6(2\times-1)]$$

$$nA_2 = \frac{1}{24}(4+8-12)$$

$$nA_2 = 0$$

$$nE = \frac{1}{24}[(4\times2)+8(1-1)+6(2\times0)]$$

$$nE = \frac{1}{24}[8-8] = 0$$

$$nE = 0$$

$$nT_1 = \frac{1}{24}[(4\times3)+8(1\times0)+6(2\times-1)]$$

$$nT_1 = \frac{1}{24}[12-12]$$

$$nT_1 = 0$$

$$nT_2 = \frac{1}{24}[4\times3+8(1\times0)+6(2\times1)]$$

$$= \frac{1}{24}[12+12]$$

$$\boxed{nT_2 = 1}$$

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$\boxed{\text{Total. R.R.} = A_1 + T_2}$

- s orbital having always A_1 symmetry.
- s orbital will transform according to A_1 symmetry.

$\boxed{\text{s orbital} = (x^2 + y^2 + z^2)}$

- P_x, P_y & P_z orbital will transform according to x, y, z axis that means T_2 symmetry.

$\boxed{p_x, p_y, p_z \text{ orbital} = x, y, z}$

- $\boxed{A_1 = \text{s orbital}}$

$\boxed{T_2 = p_x, p_y, p_z \text{ and } dxy, dxz, dyz}$

Here 2 combinations are possible i.e.

I^st Combination :

$s, p_x, p_y, p_z = sp^3$

II^nd Combination :

$s, dxy, dxz, dyz = sd^3$

$\underset{sp^3}{CH_4}$ & $\underset{sd^3}{MnO_4^{-2}}$ both having Tetrahedron structure.

Ans. (vii) In CH_4, central atom carbon have not d-orbitals, so the hybridisation is sp^3.

In MnO_4^{-2} central atom is Mn and Mn having d- orbitals and energy of d-orbital of Mn and s-orbitals are comparable as sd^3 hybridisation is fit.

Q. Which of the following combination of orbitals for hybridisation will give Tetrahe-dral symmetry?
(i) s, p_x, p_y, p_z
(ii) s, dxy, dxz, dyz
(iii) s, dz^2, dx^2-y^2, dxy
(iv) s, dxy, dyz, dz^2

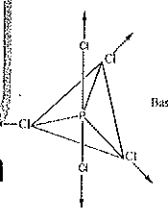
Ans. **(i) and (ii).**

Q. Consider AB_5 type trigonal bipyramid molecule with s,p and d-orbitals on the central atom. Explain the possible hybridisation scheme for the σ bond. always bond vector is use PCl$_5$

No. of unshifted bond vectors

Contribution per bond vector

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
	5	2	1	3	0	3
	1	1	1	1	1	1
R.R.	5	2	1	3	0	3



Basis: Bond vector

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order of group = 12

$$nA_1' = \frac{1}{12}\left[(5\times1)+2(2\times1)+3(1\times1)+1(3\times1)+0+3(3\times1)\right]$$

$$nA_1' = \frac{1}{12}[5+4+3+3+9] = \frac{24}{12} = 2$$

$$\boxed{nA_1' = 2}$$

$$nA_2' = \frac{1}{12}\left[(5\times1)+2(2\times1)+(3\times1\times-1)+1(3\times1)+0+3(3\times-1)\right]$$

$$nA_2' = \frac{1}{12}[5+4-3+3+0-9]$$

$$\boxed{nA_2' = 0}$$

$$nE' = \frac{1}{12}\left[(5\times2)+2(2\times-1)+3(1\times0)+1(3\times2)+0+3(3\times0)\right]$$

$$nE' = \frac{1}{12}[10-4+6]$$

$$nE' = \frac{12}{12} = 1$$

$$\boxed{nE' = 1}$$

$$nA_2'' = \frac{1}{12}\left[(5\times1)+2(2\times1)+3(1\times-1)+1(3\times-1)+0+3(3\times1)\right]$$

$$nA_2'' = \frac{1}{12}[5+4-3-3+9] = \frac{12}{12}$$

$$\boxed{nA_2'' = 1}$$

For Checking :

A_1'	1	1	1	1	1	1
A_1'	1	1	1	1	1	1
A_2''	1	1	−1	−1	−1	1
E'	2	−1	0	+2	−1	0
Total	5	2	1	3	0	3

Total = $2A_1' + A_2'' + E'$

A_1' A_2'' E'

s p_z p_x, p_y

dz^2 dx^2-y^2, dxy

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Possible Combinations : www.careerendeavour.com

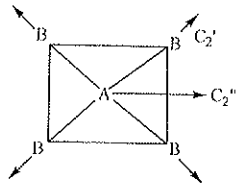
$sp^3d \rightarrow s, p_z, p_x, p_y, dx^2-y^2$

$sp^3d \rightarrow s, p_z, p_x, p_y, dxy$

$spd^3 \rightarrow s, dz^2, p_z, dx^2-y^2, dxy$

$sp^3d \rightarrow s, p_z, p_x, p_y, dz^2$

Q. Consider AB_4 square planar & give suitable hybridisation in it.



D_{4h}	E	$2C_4$	C_2	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$
Number of unshifted bond vector	4	0	0	2	0	0	0	4	2	0
Countribution per bond vector	1	1	1	1	1	1	1	1	1	1
R.R	4	0	0	2	0	0	0	4	2	0

$$nA_{1g} = \frac{1}{16}\left[(4\times1)+2(2\times1)+(4\times1)+2(2\times1)\right]$$
$$= \frac{1}{16}(4+4+4+4)$$
$$= \frac{16}{16} = 1$$

$$nB_{1g} = \frac{1}{16}\left[4\times1+2(2\times1)+(4\times1)+2(2\times1)\right]$$
$$= \frac{1}{16} = 1$$

$$nE_u = \frac{1}{16}\left[(4\times1)+2(2\times0)+(4\times2)+2(2\times0)\right]$$
$$nE_u = \frac{16}{16} = 1$$

Total Reducible form = $\boxed{A_{1g} + B_{1g} + E_u}$

For Checking :

A_{1g}	1	1	1	1	1	1	1	1	1	1
B_{1g}	1	1	1	1	−1	1	1	1	1	−1
E_u	2	0	−2	0	0	−2	0	2	0	0
Total	4	0	0	2	0	0	0	4	2	0

A_{1g}	B_{1g}	E_u
s	dx^2-y^2	p_x, p_y
dz^2		

POSSIBLE HYBRIDISATION :

$sp^2d \rightarrow$ s, dx^2-y^2, p_x, p_y

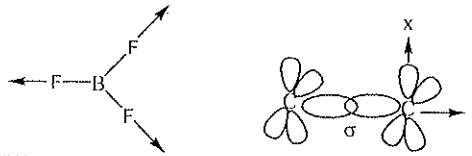
$spd^2 \rightarrow$ s, dx^2-y^2, dz^2, p_x

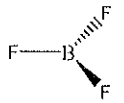
$spd^2 \rightarrow$ s, dx^2-y^2, dz^2, p_y

$p^2d^2 \rightarrow$ p_x, p_y, dx^2-y^2, dz^2 } not possible

Q. BF_3 molecule (D_3h) calculate π bond

Basis set – 2N coordinate :





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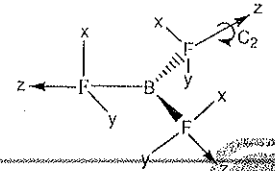
D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
No. of un-shifted vector	3	0	1	3	0	1
contribution per vector	2	−1	−2	0	−1	0
R.R.	6	0	−2	0	0	0

Basis set 2N cordination because one coordinate use in the σ bond but π bond always form perpendicular to the σ bond



$$E = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

identity = 2

$$C_3 = \begin{bmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{bmatrix} \quad x = -1$$

For 2 N Coordinate :

E $\quad \begin{vmatrix} 1 & 0 \\ 0 & 1 \end{vmatrix}$ $\quad x = 2$

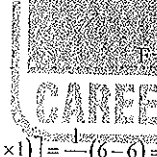
C_3 $\quad \begin{vmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$ $\quad x = -1$

C_2 $\quad \begin{vmatrix} -1 & 0 \\ 0 & -1 \end{vmatrix}$ $\quad x = -2$

S_3 $\quad \begin{vmatrix} -\frac{1}{2} & \frac{\sqrt{3}}{2} \\ -\frac{\sqrt{3}}{2} & -\frac{1}{2} \end{vmatrix}$ $\quad x = -1$

σ_h $\quad \begin{vmatrix} -1 & 0 \\ 0 & 1 \end{vmatrix}$ $\quad x = 0$

σ_v $\quad \begin{vmatrix} 1 & 0 \\ 0 & -1 \end{vmatrix}$ $\quad x = 0$



$$nA_1' = \frac{1}{12}\left[6\times1+3(-2\times1)\right] = \frac{1}{12}(6-6) = 0$$

$$nA_2' = \frac{1}{12}\left[(6\times1)+3(-2\times-1)\right] = \frac{12}{12} = 1$$

$$nE' = \frac{1}{12}\left[(6\times2)+3(-2\times0)\right] = \frac{12}{12} = 1$$

$$nA_1'' = \frac{1}{12}\left[(6\times1)+3(-2\times1)\right] = \frac{0}{12} = 0$$

$$nA_2'' = \frac{1}{12}\left[(6\times1)+3(-2\times-1)\right] = \frac{12}{12} = 1$$

$$nE'' = \frac{1}{12}\left[(6\times2)+3(-2\times0)\right] = \frac{12}{12} = 1$$

$\boxed{\text{Total} = A_2' + E' + A_2'' + E''}$

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A_2'	E'	A_2''	E''
↓	↓	↓	↓
No.	p_x, p_y	p_z	dxz, dyz
any orbital	dx^2-y^2, dz^2		

ORBITAL USED FOR σ BONDING : 3N COORDINATE

$A_1' + E'$

↓	↓
s	p_x, p_y
dz^2	dx^2-y^2, dxy

Orbitals for π bonding : $A_2' + E' + A_2'' + E''$ possible.

- E' orbital will involve in σ bonding (p_x, p_y)
- A_2' does not have any orbitals
- E" has dxy and dyz orbital which are absent on boron atom because Boron is p-block element.
- Only A_2'' orbital P_z is available for π bonding in BF_3.

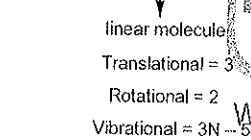
  The B–F bond length in BF_3 is shorter than B–F single bond & larger than B–F double bond. that indicates the resonance of 1π bond between three B–F bond in BF_3.

π - BONDING IN MnO_4^-, MCl_4^{-2} :

Only d-orbital having metal give π bond with sp^3 (Td) hybridization.

Basis set : 2N Coordinate

Td	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of unshifted atom	4	1	0	0	2
Countribution per atom	2	1	2	0	0
R.R.	8	1	0	0	0



$$nA_1 = \frac{1}{24}\left[(8\times1)+8(-1\times1)\right] = 0$$

$$nA_2 = \frac{1}{24}\left[8\times1+8(-1\times1)\right] = 0$$

$$nE = \frac{1}{24}\left[8\times2+8(-1\times-1)\right] = \frac{24}{24} = 1$$

$$nT_1 = \frac{1}{24}\left[8\times3+8(-1\times0)\right] = \frac{24}{24} = 1$$

$$nT_2 = \frac{1}{24}\left[8\times3+0\right] = 1$$

$$\text{Total} = E + T_1 + T_2$$

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For σ

	$A_1 + T_2$	} σ bond	$E = dz^2, dx^2-y^2$
sp^3 →	s, p_x, p_y, p_z		T_1 = no orbital
→	s, dxy, dyz^2, dzx.		$T_2 = p_x\ p_y\ p_z$ } σ dxy, dyz, dxz

} π bond

According to the transformation properties of obtain information.

- It is impossible to form a complete set of π bonds, because there are no orbitals on atom A of T_1 symmetry.
- The π bond will not be independent of σ bond since T_2 orbital require for both.
- There are 2 sets of T_2 type orbital. Thus it is possible to have both σ and π bond from the T_2 symmetry orbitals. But the mixing of orbitals will depend on specific case.

Example: In case of CH_4, T_2 orbital will involve in σ bonding and E orbitals and T_2 orbitals are not available on C-atom. Hence p-bonding is not possible.

But in the case of MCl_4^{-2} type complex compound the 3 of the T_2 orbitals and E orbitals can involve into the π bonding. Hence according to symmetry rule the maximum possible no. of π bond in Tetrahedron are 5.

I.R. and Raman Spectroscopy Explain by Group Theory

Q. Consider a AB_2 type bent molecule (H_2O) i.e. v-shape molecule. Find out the I.R. and Raman active vibration using the symmetry rules. The character table of C_{2v} point group given.

(1) Derivation of Reducible representation using 3N coordinate as basis set.

(2) Reduction of Reducible representation. This will give 3N degree of freedom.

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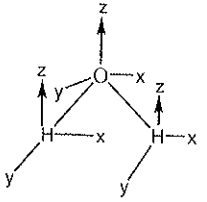
(3) Removal of Translational & Rotational degree of freedom to get vibration degree of freedom

(4) Translational properties of vibrations according to I.R. and Raman spectroscopy.

(5) Drawing of vibrations.

$C_{2v}(H_2O)$	E	C_2	σ_{xy}	σ_{yz}
Number of unshifted atom	3	1	3	1
Contribution per atom	3	–1	1	1
R.R.	9	–1	3	1



$$nA_1 = \frac{1}{4}\left[(9\times1)+(-1\times1)+(3\times1)+(1\times1)\right] = \left[\frac{9-1+3+1}{4}\right] = \frac{12}{4} = 3$$

$$nA_2 = \frac{1}{4}\left[(9\times1)+(-1\times1)+(3\times-1)+(1\times-1)\right] = \frac{4}{4} = 1$$

$$nB_1 = \frac{1}{4}\left[(9\times1)+(-1\times-1)+(3\times1)+(1\times-1)\right] = \frac{12}{4} = 3$$

$$nB_2 = \frac{1}{4}\left[(9\times1)+(-1\times-1)+(3\times-1)+(1\times-1)\right] = \frac{8}{4} = 2$$

$\boxed{\text{Total} = 3A_1 + A_2 + 3B_1 + 2B_2}$

Rotational degree of freedom transform according to R_x, R_y & R_z

Translational degree of freedom transform according to x, y & z.

$R_x - B_2$ $\quad x = B_1$

$R_y - B_1$ $\quad y = B_2$

$R_z - A_2$ $\quad z = A_1$

$\boxed{\text{Vibrational} = 2A_1 + B_1}$ Three degree of freedom.

(6) I.R. active vibrations transforms according to 3 cartecian coordinate x, y, z.

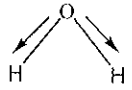
(7) Raman active vibration transforms according to the quadratic function of x, y, z.

$A_1 = z, x^2, y^2, z^2$ I.R. as well as Raman active.

$B_1 = x, xz$ I.R. and Raman active both.

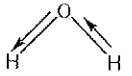
H_2O	E	C_2	σ_{xz}	σ_{yz}
A_1	1	1	1	1

means all vibrations are symmetric.



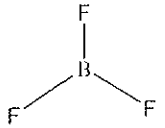
H_2O	E	C_2	σ_{xz}	σ_{yz}
B_1	1	−1	1	−1

means vibrations are assymmetric



Q. Explain I.R. & Raman active vibration in BF_3 molecule.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
Number of unshifted atom	4	1	2	4	1	2
Contribution	3	0	−1	1	−2	1
R.R.	12	0	−2	4	−2	2



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$$nA_1' = \frac{1}{12}\left[(12\times1)+3(-2\times1)+(4\times1)+2(-2\times1)+3(2\times1)\right]$$

$$nA_1' = \frac{1}{12}\left[12-6+4-4+6\right] = 1$$

$$nA_1' = 1$$

$$nA_2' = \frac{1}{12}\left[(12\times1)+3(-2\times1)+(4\times1)+2(-2\times1)+3(2\times-1)\right]$$

$$nA_2' = \frac{1}{12}\left[12-6+4-4-6\right] = \frac{0}{12} = 0$$

$$nA_2' = 0$$

$$nE' = \frac{1}{12}\left[(12\times2)+3(-2\times0)+(4\times2)+2(-2\times-1)+3(2\times0)\right]$$

$$nE' = \frac{1}{12}\left[24+0+8+4+0\right]$$

$$nE' = \frac{1}{12}\times36$$

$$nE' = 3$$

$$nA_1'' = \frac{1}{12}\left[(12\times1)+3(-2\times1)+(4\times-1)+2(-2\times-1)+3(2\times-1)\right]$$

$$= \frac{1}{12}\left[12-6-4+4-6\right]$$

$$nA_1'' = 0$$

$$nA_2'' = \frac{1}{12}\left[(12\times1)+3(-2\times-1)+(4\times-1)+2(-2\times-1)+3(2\times1)\right]$$

$$nA_2'' = \frac{1}{12}\left[12+6-4+4+6\right]$$

$$nA_2'' = \frac{24}{12} = 2$$

$$nA_2'' = 2$$

$$nE'' = \frac{1}{12}\left[(12\times2)+3(-2\times0)+(4\times-2)+2(-2\times1)+3(2\times0)\right]$$

$$= \frac{1}{12}\left[24-8-4\right]$$

$$nE'' = \frac{12}{12} = 1$$

$$nE'' = 1$$

$\boxed{\text{Total} = A_1' + A_2' + 3E' + 2A_2'' + E''}$

$R_x - A_2'$ $\quad x - E'$

$R_y - E''$ $\quad y - E'$ $\Big]E'$

$R_z - E''$ $\quad z - A_2''$ $\Big]E''$

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$A_1' + A_2' + 3E' + 2A_2'' + E''$
$\downarrow \quad \downarrow \quad \downarrow \quad \downarrow \quad \downarrow$
$\checkmark \quad \times \quad 2\text{ use} \quad 1\text{ use} \quad \times$

left $A_1' + E' + A_2''$

R.R. vib. $= A_1' + 2E' + A_2''$

$A_1' \rightarrow x^2 + y^2, z^2$ Raman active only
$A_2'' \rightarrow z$ I.R. active only
$E' \rightarrow x, y, x^2 - y^2, xy$ I.R. & Raman active both.

In Plane vibration – symmetrical w.r.t. σ_h

A_1' and E'

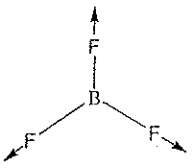
out of plane vibration – A_2''

II Vibration → symmetric w.r.t. to p-axis.

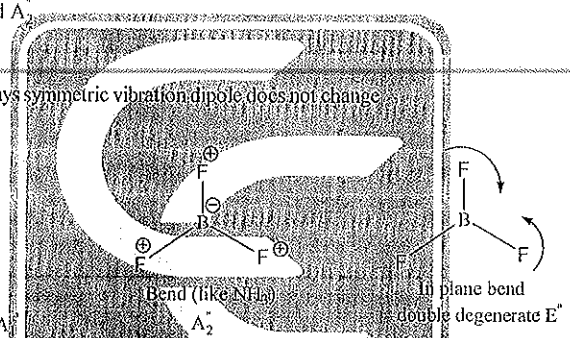
A_1' and A_2''

⊥ vibration → E'

DRAWING : A_1' always symmetric vibration dipole does not change



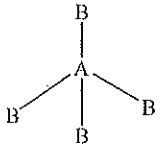
symmetric streching A_1'



In plane bend
double degenerate E''

TETRAHEDRON : Basis set = 3N coordinate

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of unshifted atom	3	0	1	1	3
Contribution per atom	3	0	−1	−1	1
R.R.	15	0	−1	−1	3



$$nA_1 = \frac{1}{24}\left[(15\times1)+3(-1\times1)+6(-1\times1)+6(3\times1)\right]$$
$$nA_1 = \frac{1}{24}[15-3-6+18]$$
$$nA_1 = 1$$
$$nA_2 = \frac{1}{24}\left[(15\times1)+3(-1\times1)+6(-1\times-1)+6(3\times-1)\right]$$
$$nA_2 = \frac{1}{24}[15-3+6-18]$$
$$nA_2 = 0$$

$$nE = \frac{1}{24}\left[(15\times2)+3(-1\times2)+6(-1\times0)+6(3\times0)\right]$$
$$nE = \frac{1}{24}[30-6]$$
$$nE = 1$$

$$nT_1 = \frac{1}{24}\left[(15\times3)+3(-1\times-1)+6(-1\times1)+6(3\times-1)\right]$$
$$nT_1 = \frac{1}{24}[45+3-6-18]$$
$$nT_1 = 1$$

$$nT_2 = \frac{1}{24}\left[(3\times15)+3(-1\times-1)+6(-1\times-1)+6(3\times1)\right]$$
$$nT_2 = \frac{1}{24}[45+3+6+18]$$
$$nT_2 = 3$$

$\boxed{\text{Total} = A_1 + E + T_1 + 3T_2}$

A_1	E	T_1	T_2
↓	↓	↓	↓
s	dx^2-y^2	no orbital	$p_x p_y p_z$

POSSIBLE HYBRIDISATION :

$sp^2d \rightarrow s, p_x, p_y, dx^2-y^2$
$sp^2d \rightarrow s, p_y, p_z, dx^2-y^2$
$sp^2d \rightarrow s, p_x, p_z, dx^2-y^2$

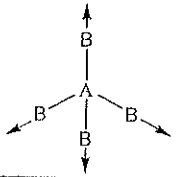
I.R. and Raman Active Vibration in Td :

$x - T_2$, $y - T_2$, $z - T_2$ } T_2 → $R_x = T_1 \times T_2$, $R_y = T_1 \times T_2$, $R_z = T_1 \times T_2$

$A_1 + E + T_1 + 3T_2$
$\checkmark \quad \checkmark \quad \downarrow \quad \downarrow$
$\quad\quad\quad\quad \times \quad 2T_2\text{left}$

$A_1 \rightarrow x^2+y^2+z^2$ → Raman active
$E \rightarrow 2z^2-x^2-y^2, x^2-y^2$ → Raman active
$T_2 \rightarrow x, y, z, [xy, xz, yz]$ → I.R. and Raman active both.

Drawing : A_1 give symmetric vibration



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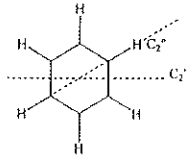
Q. **Benzene is a good example of a important molecule with relatively high symmetry (D_6h)**

(a) **Determine the symmetry type of the vibrations.**

(b) **Determine the activities of each type of vibrations.**

(c) **classify all in plane and out of plane vibrations**

(d) **classify the ∥ and ⊥ vibrations.**



Basis set – 3N coordinate

D_{6h}	E	$2C_6$	$2C_3$	$C_2 \left(=C_6^3\right)$	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
Number of unshifted atom	12	0	0	0	4	0	0	0	0	12	0	4
Contribution per atom	3	2	0	−1	−1	−1	−3	−2	0	1	−1	−1
R.R.	36	0	0	0	−4	0	0	0	0	12	0	−4

Number of classes = 12

order of D_{6h} point group = 24

$$nA_{1g} = \frac{1}{24}\left[(36\times1)+3(-4\times1)+(12\times1)+3(4\times1)\right] = 36-12+12+12 = 2$$

$$nA_{2g} = \frac{1}{24}\left[36+12+12-12\right] = 2$$

$$nB_{1g} = \frac{1}{24}\left[36-12-12-12\right] = 0$$

$nB_{2g} = 2$

$nE_{1g} = 2$

$nE_{2g} = 4$

$nA_{1u} = 2$

$nA_{2u} = 0$

$n_{B_{1u}} = 2$

$nB_{2u} = 2$

$nE_{1u} = 4$

Streching – only bond length change

Bending – only bond angle change

$$\begin{matrix} x-E_{1u} \\ y-E_{1u} \\ z-A_{2u} \end{matrix}\Bigg] E_{1u} \qquad \begin{matrix} R_X-E_{1g} \\ R_y-E_{1g} \\ R_z-A_{2g} \end{matrix}\Bigg] E_{1g}$$

$$R.R. \rightarrow 2A_{1g}+2A_{2g}+2B_{2g}+2E_{1g}+4E_{2g}+2A_{1u}+2B_{1u}+2B_{2u}+4E_{1u}+2E_{2u}$$

(↓ 1 left; ↓ 1 left; ↓ 3 left)

$$\text{left R.R.} \rightarrow 2A_{1g}+A_{2g}+2B_{2g}+E_{1g}+4E_{2g}+2A_{1u}+2B_{1u}+2B_{2u}+3E_{1u}+2E_{2u}$$

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$$\begin{cases} A_{1g} - \text{Raman only in plane} \parallel & E_{2g} \rightarrow \text{Raman only in plane} \perp \\ A_{2g} - \times & A_{2g} \rightarrow \text{I.R.only outofplane} \parallel \\ B_{2g} - \times & E_{1u} \rightarrow \text{I.R. only in plane} \parallel \\ E_{1g} - \text{Raman out plane} \parallel & \end{cases}$$

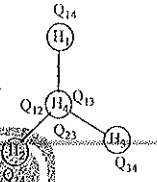
Here the I.R. vibrations are not Raman active & Raman active vibrations are not I.R. active So prove that principle of **mutual exclusion of vibration.**

Q. * To find the streching vibration use bond vector as basis set

* To find the bending vibration use bond angle as basis set

Basis set → Bond angle

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of shifted angle	6	0	2	0	2
Contribution per angle	1	1	1	1	1
R.R.	6	0	2	0	2



$$nA_1 = \frac{1}{24}\left[(6\times1)+3(2\times1)+6(2\times1)\right]$$

$$nA_1 = \frac{1}{24}\left[6+6+12\right] = 1$$

$$nA_2 = \frac{1}{24}\left[(6\times1)+3(2\times1)+6(2-1)\right]$$

$$nA_2 = \frac{1}{24}\left[6+6-12\right] = 0$$

$$nE = \frac{1}{24}\left[(6\times2)+3(2\times2)+6(2\times0)\right] = 1$$

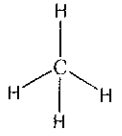
$$nT_1 = \frac{1}{24}\left[6\times3+3(2\times-1)+6(2\times1)\right] = 0$$

$$nT_2 = \frac{1}{24}\left[6\times3+3(2\times-1)+6(2\times1)\right] = 1$$

$$\boxed{R.R. = A_1+E+T_2}$$

Basis set – bond Vector

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of shifted angle	4	1	0	0	2
Contribution per angle	1	1	1	1	1
R.R.	4	1	0	0	2



$$\boxed{R.R. = A_1+T_2}$$

Basis set – 3N coordinate

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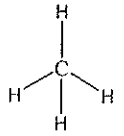
T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
Number of shifted angle	5	2	1	1	3
Contribution per angle	3	0	−1	−1	1
R.R.	15	0	−1	−1	3



$3N = A_1 + E + T_1 + 3T_2$

$I.R. = A_1 + E + 2T_2$.

The vibrational symmetries according to 3N coordinates are A_1, E & T_2 by according to the bond length which explain streching vibrations the symmetry types are A_1 & T_2 & by bond angle the which explains the bending vibrations the symmetries are A_1, E & T_2. If we compare the total dimensionality of streching and bending vibrations we can see there is one extra A_1 representation

- In case of streching the A_1 vibration explain the brief vibration in which all the bond length increases or decreases simultaneously
- In case of bending vibration the A_1 symmetry explains increase or decrease all 6 bond angle simultaneously which is totally impossible. Hence we can say that A_1 vibration of CH_4 consists of purely C–H streching.

Q. Find the Raman and I.R. active vibrations in AB_6 type molecule having octahedral Geometry.

Ans. Basis set : 3N coordinate

Oh	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Number of unshifted atom	7	1	1	3	3	1	1	1	5	3
Contribution per atom	3	0	−1	1	−1	−3	−1	0	1	1
R.R	21	0	−1	3	−3	−3	−1	0	5	3

$$nA_{1g} = \frac{1}{48}\left[(21\times1)+6(-1\times1)+6(3\times1)+3(-3\times1)+(-3\times1)+6(-1\times1)+3(5\times1)+6(3\times1)\right]$$

$$nA_{1g} = 1$$

$$nE_g = \frac{1}{48}\left[(21\times2)+6(-1\times0)+6(3\times0)+3(-3\times2)+(-3\times2)+6(-1\times0)+3(5\times2)+6(3\times0)\right]$$

$$nE_g = 1$$

$$nT_{1g} = \frac{1}{48}\left[(21\times3)+(6\times-1\times-1)+6(3\times1)+3(-2\times-1)+(-3\times3)+6(-1\times1)+3(5\times-1)+6(3\times-1)\right]$$

$$nT_{1g} = 1$$

$$nT_{2g} = \frac{1}{48}\left[(21\times3)+6(-1\times1)+6(3\times-1)+3(-2\times-1)+(-3\times3)+6(-1\times-1)+3(5\times-1)+6(3\times1)\right]$$

$$nT_{2g} = 1$$

$$nT_{1u} = \frac{1}{48}\left[(21\times3)+6(-1\times-1)+6(3\times1)+3(-2\times-1)+(-3\times-3)+6(-1\times-1)+3(5\times1)+6(3\times1)\right]$$

$$nT_{1u} = 3$$

$$nT_{2u} = \frac{1}{48}\left[(21\times3)+6(-1\times1)+6(3\times-1)+3(-2\times-1)+(-3\times-3)+6(-1\times1)+3(5\times1)+6(3\times-1)\right]$$

$$nT_{2u} = 1$$

$$\text{Total} = A_{1g} + E_g + \underset{\times}{T_{1g}} + T_{2g} + \underset{\text{2 left}}{3T_{1u}} + T_{2u}$$

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$$\left.\begin{matrix}x-\\y-\\z-\end{matrix}\right\}T_{1u} \qquad \left.\begin{matrix}R_x-\\R_y-\\R_z-\end{matrix}\right\}T_{1g} \qquad \text{left total} = A_{1g} + E_g + T_{2g}2T_{1u} + T_{2u}$$

Here

A_{1g}	→	$x^2+y^2+z^2$	Raman active
E_g	→	$2z^2-x^2-y^2, x^2-y^2$	Raman active
T_{2g}	→	x^2, y^2, xy	Raman active
T_{1u}	→	x, y, z	I.R. active

Symmetric octahedron also follow "Mutual Exclusion Principle" it means "vibrations those are Raman active are I.R. inactive & I.R. active vibration are Raman inactive.

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